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RUBBER CHEMISTRY AND TECHNOLOGY

PUBLISHED QUARTERLY BY THE
DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY

KOSMOS 60

Kosmos 60 is today the most talked about furnace black for reinforcing natural and synthetic rubber. It originates from oil, and its manufacture is scientifically controlled to meet the highest standards. Its superb processing and balance of strength make for the best in rubber products.

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Charleston 27, W. Va.

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Call on PHILBLACK® for valuable information about carbon blacks!

We've been in the carbon black business for many years. In fact, Phillips pioneered the improved furnace blacks which have contributed so significantly to the manufacture of better rubber products. During this time we have collected important data on rubber and worked out many solutions to rubber problems.

Maybe you'd like more data on how to speed up processing . . . improve extrusions and moldings . . . increase flex life? It is our business to help rubber manufacturers turn out better products . . . more easily and more profitably.

To take advantage of the helpful services available to you, consult your Phillips technical representative.

Meet the Philblacks!

DISCOVER WHAT THEY'LL DO FOR YOU!

A — **Philblack A FEF Fast Extrusion Furnace Black**
Ideal for smooth tubing, accurate molding, satiny finish. Mixes easily. High, hot tensile. Disperses heat. Non-staining.

I — **Philblack I ISAF Intermediate Super Abrasion Furnace Black**
Superior abrasion resistance at moderate cost. Very high resistance to cuts and cracks. More tread miles at high speeds.

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For long, durable life. Good electrical conductivity. Excellent flex. Fine dispersion.

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Toughest black on the market. Extreme abrasion resistance. Withstands aging, cracking, cutting and chipping.

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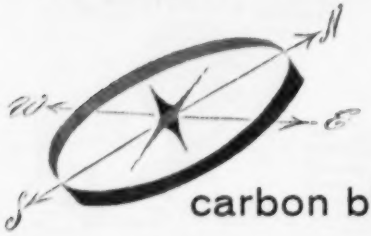
PHILLIPS CHEMICAL COMPANY, Rubber Chemicals Division, 318 Water St., Akron 8, Ohio.
Export Sales: 80 Broadway, New York 5, N. Y.
West Coast: Harwick Standard Chemical Company, Los Angeles, California.

Entered as second-class matter March 19, 1943, at the Post Office at Lancaster, Pa., under the Act of August 24, 1912. Acceptance for mailing at special rate of postage provided for in paragraph (d-2), Section 34.40, P. L. and R. of 1948, authorized September 25, 1940.

WITCO-CONTINENTAL



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Technical assistance has always played an important part in Witco-Continental's service. At our Akron laboratory, experienced rubber chemists are available to assist in solving customers' problems. At our modern research laboratory in Amarillo, new types of blacks are constantly being developed to help the rubber industry meet demands for new and improved products.

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SA 57-3
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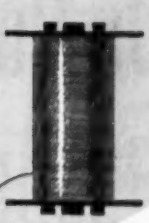
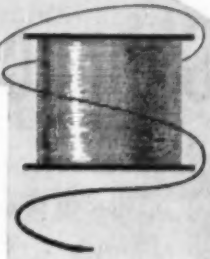


Extra Fine
Extra Clean



* The extra fine grade of these Sharples Accelerators is designed primarily for use in cut rubber thread and thin-wall insulated wire compounds where maximum freedom from foreign material is essential.

Samples available upon request.

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ELA—Elastomer lubricating agent

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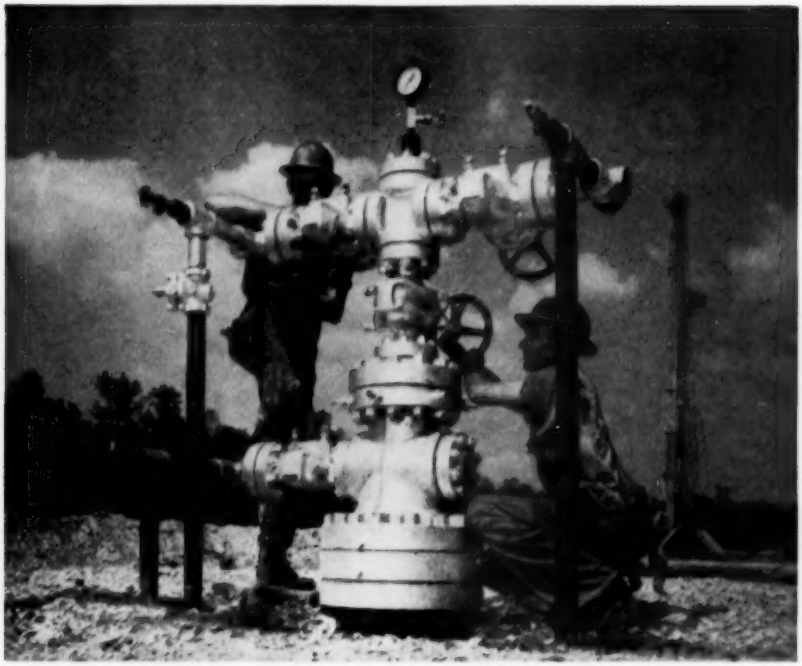

Something new under the Christmas tree

The "tree" is the complex system of valves, fittings and gauges that controls the flow of oil from wells. What's new is the blend of CHEMIGUM and PLIOFLEX being used in the soles of the oil workers' shoes.

CHEMIGUM is a nitrile rubber. PLIOFLEX is a styrene rubber. Both have been used separately in high-grade soles of various types. Now, they can be blended to give stocks better in combined oil-resistance and wearing properties than those of other rubbers or blends—and at much lower cost. Other advantages are: Low specific gravity. Excellent low temperature properties. Ease of processing. Safe scorch values. Excellent bin aging.

CHEMICAL GOODYEAR DIVISION

Rubber & Rubber Chemicals Department

Why not learn more about CHEMIGUM/PLIOFLEX blends for shoe soles or any oil-resistant product? Write for details plus the latest *Tech Book Bulletin* to:

Goodyear, Chemical Division, Akron 16, Ohio

Chemigum, Plioflex, Pliolite, Plio-Tuf, Pliovic—T. M.'s The Goodyear Tire & Rubber Company, Akron, Ohio

CHEMIGUM • PLIOFLEX • PLIOLITE • PLIO-TUF • PLIOVIC • WING-CHEMICALS

High Polymer Resins, Rubbers, Latices and Related Chemicals for the Process Industries

Announcing VA-7

... an economical vulcanizing agent for heat-resistant, non-blooming stocks

VA-7 is a new liquid vulcanizing agent for all types of unsaturated elastomers. It provides economical "sulfurless" cures for nitrile, GR-S and natural rubber stocks.

Stocks compounded with VA-7 display an outstanding combination of heat aging resistance . . . . high tensile strengths . . . . good hot compression set resistance . . . . and non-blooming characteristics in the cured and uncured states.

VA-7 also offers processing advantages—it can be dispersed more easily and uniformly than sulfur. Stable emulsions for curing latices can easily be prepared from VA-7.

The moderate price of VA-7 is another feature that makes this product worth your investigation. *Try VA-7 for heat-resistant, non-blooming stocks at reasonable cost!*

For compounding information and a sample of VA-7 fill out and mail the handy coupon.

CHECK LIST OF VA-7 PROPERTIES

Outstanding heat aging resistance
Non-blooming in cured or uncured state
High strengths at low concentrations
Easy and uniform dispersion
Good hot compression set
Moderate price

THIOKOL CHEMICAL CORPORATION
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Trenton 7, New Jersey

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and a sample of VA-7 ☐

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—a new trademark character we've adopted to represent our PHILPRENE® Polymers and Masterbatches.

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PHILLIPS CHEMICAL COMPANY

Rubber Chemicals Division, 318 Water Street, Akron 8, Ohio

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TEXAS CHANNEL BLACKS are manufactured in the world's largest channel black plant. With our own natural resources nearby we assure you continuing deliveries to fill your requirements.

TEXAS CHANNEL BLACKS

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Looking for a cost cutting, quality building miracle additive?

USE **VELSICOL**

hydrocarbon resins to make better rubber products, build quality and cut costs!

Here are the facts!

PHYSICAL PROPERTIES	GE-9	AB-11-4	X-30
Type	Thermoplastic Hydrocarbon	Thermoplastic Hydrocarbon	Thermoplastic Hydrocarbon
Form	Solid or Powder	Solid or Flaked	Solid or Flaked
Specific Gravity @ 60°F	1.13-1.15	1.09-1.02	——
Weight per gallon @ 60°F (lbs.)	9.41-9.58	9.08-9.33	——
Bulking Value @ 60°F.	0.1044-0.1052	0.1074-0.1102	——
Softening Point (Ball and Ring)	220°-230°F	220°-230°F	210°-220°F
Color (Coal Tar Scale)	20-22	3½-4½	1½-2*
Acid No.	0-2	0-2	0-2
Saponification No.	0-2	0-2	0-2

*Color: Gardner: 10-11; Rosin Scale: I-K.

These resins also have exceptionally good electrical insulation properties, because they are hydrocarbon polymers. Compatible with a variety of natural and synthetic rubber compounds.

FOR: battery cases, electrical insulation, rubber shoe soles and heels, rubber floor tiling, gaskets and jar rings, hard rubber compounds, tubular compounds, mechanical goods, rubber adhesives and cements, reclaimed rubber, molded rubber products, colored rubber stocks.

ADVANTAGES: better milling, calendering, and tubing; more uniform cures, non-scorchy stocks; greater toughness, hardness, resistance to tearing, aging and abrasion; improved tensile strength and elongation; lower raw materials costs.

Write for Technical Bulletin 218.

VELSICOL
CHEMICAL CORPORATION
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VELSICOL

PANAREZ HYDROCARBON RESINS

improve products like these:

Shoe soles

Floor tile

Wire covering

Tires

If you compound rubber it will pay you to investigate *low cost* PANAREZ hydrocarbon resins. These softeners are available in any color from Barrett No. 1 to 1[illegible], and softening point from 40° F to 300° F. They are supplied in flaked or solid form.

Compounds containing Panarez resins show **IMPROVED COLOR AND COLOR STABILITY . . . IMPROVED EXTRUDABILITY . . . IMPROVED FLEX CRACK PERFORMANCE and ABRASION RESISTANCE . . . IMPROVED OZONE RESISTANCE . . . IMPROVED TEAR RESISTANCE, TENSILE STENGTH and ELONGATION.**

No change in compounding technique is required when switching to Panarez resins.

For confidential information about how these low cost resins might be helpful in your business, write us, telling the intended application.

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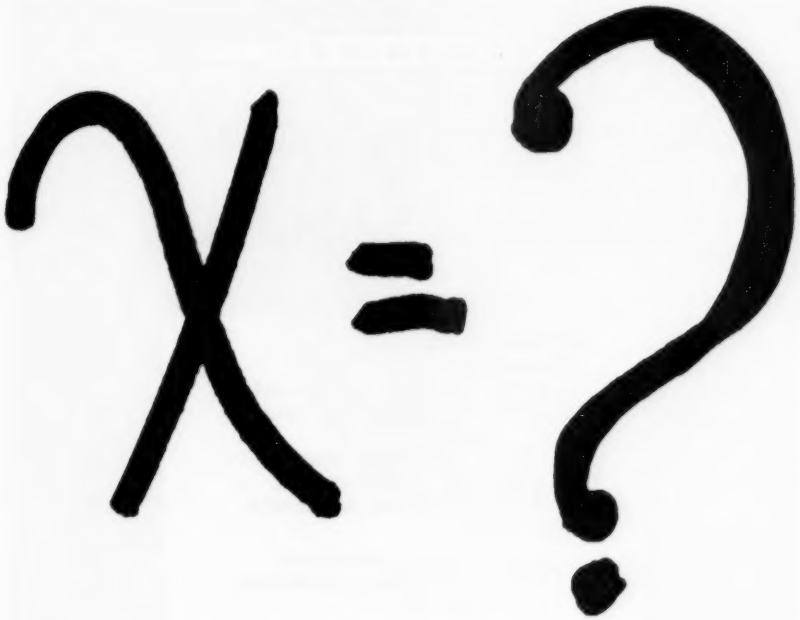
HYDROCARBON PANAREZ RESINS

PANAPOL Hydrocarbon drying oils

PANASOL Aromatic solvents



Answering Questions About Rubber Formulations Is Our Business

Sometimes the answers are so simple, we are surprised ourselves! Like the time a certain rubber processor brought us this one:

The Problem: What is the best non-staining antioxidant for a 55 Durometer natural rubber stock with a heavy whiting load?

Here's What Monsanto Compounders Did: Compounded a pale crepe stock with 100 parts of whiting . . . added Santowhite Crystals and also test batches including two other good commercial antioxidants.

The Results: Formulation with Santowhite Crystals showed best aging by a wide margin.

Better performance is the only way we sell. Sure, our crystals and powders are pure and pretty. But customers buy our rubber chemicals because they work not only in the laboratory, but on the production line.

Be your tonnage large or not-so-large, ask your questions anyhow. Unless your problem is so unique that it stumps the experts, the answer might require no more than riffling through the index of the more than 18,000 lab reports in our files. *Monsanto Chemical Company, Rubber Chemicals Dept. RC-1, (telephone HEmlock 4-1921), Akron, O.*

Santowhite: Reg. U. S. Pat. Off.

Accelerators • For fast, slow, and regulated rates of safe cure.

Antioxidants • For maximum oxidation resistance.

Specialty Compounds • For special processing problems.

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for highest quality

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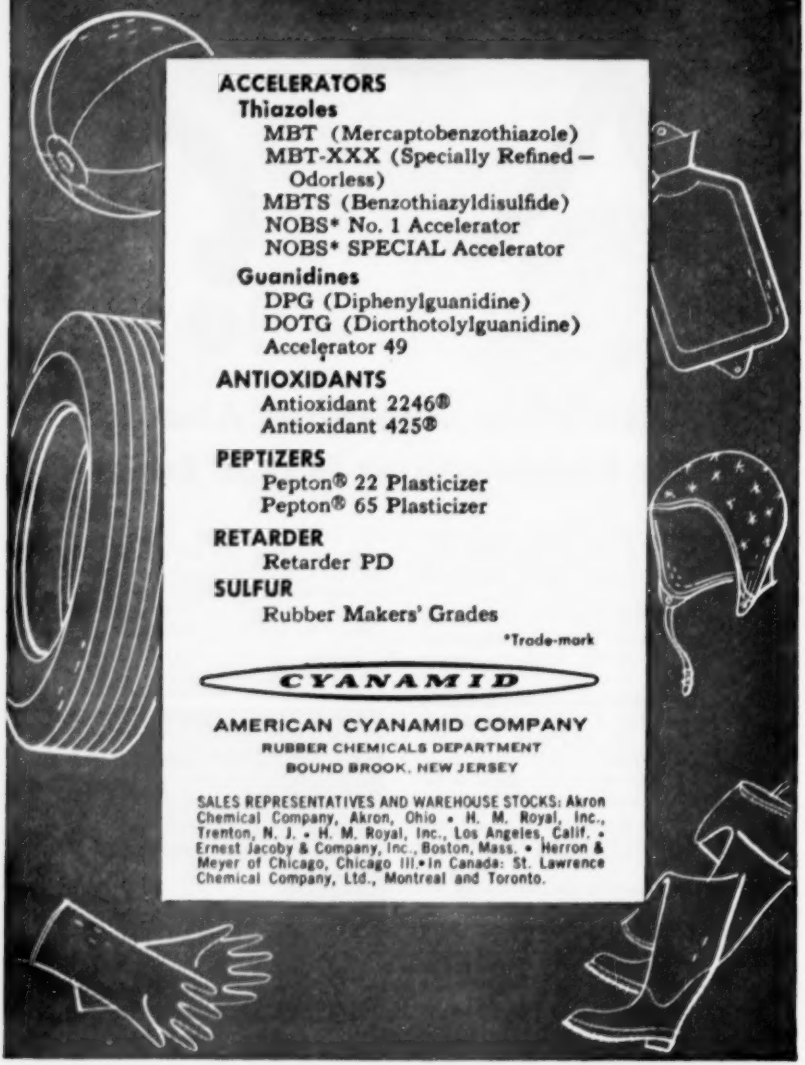

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MBT-XXX (Specially Refined—Odorless)
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NOBS* No. 1 Accelerator
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DPG (Diphenylguanidine)
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Accelerator 49

ANTIOXIDANTS

Antioxidant 2246®
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Pepton® 22 Plasticizer
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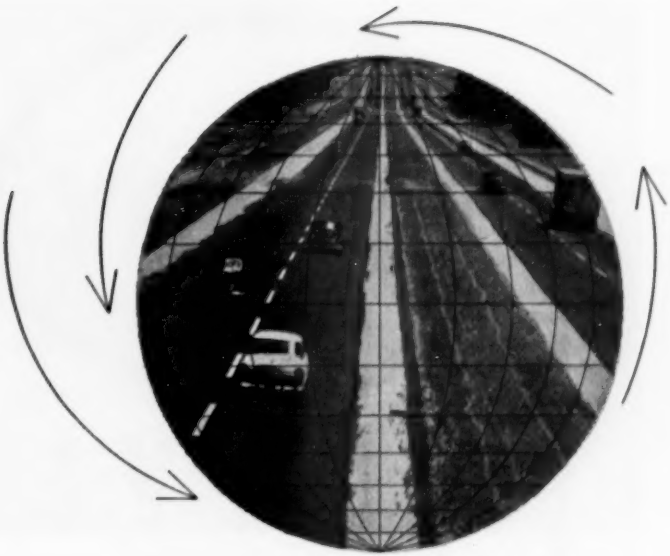

Around the World Mileage

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CHANNEL · FURNACE · THERMAL

For MAXIMUM RUBBER MILEAGE, whether in tires or in other rubber goods, Cabot offers the best quality, greatest variety of carbon blacks available. As the world's only manufacturer of a complete range of channel, furnace and thermal blacks, Cabot is able to offer a black to satisfy your every rubber requirement. That's why leading manufacturers of all types of rubber products continue to specify Cabot. For best carbon black performance, ask for . . .

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Channel Blacks

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Furnace Blacks

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Furnace and Thermal Blacks

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Enjay Butyl is the super-durable rubber with outstanding resistance to aging • abrasion • tear • chipping • cracking • ozone and corona • chemicals • gases • heat • cold • sunlight • moisture

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Here are some of the reasons for the rapidly increasing acceptance of Enjay Butyl for more and more rubber applications in more and more industries.

- Molded mechanical goods like body bumpers and auxiliary springs, outperform those made of natural rubber or GR-S types.
- Good hot tear resistance reduces percentage of mold removal rejects, thus reduces costs.
- Excellent adhesion is obtained to fabrics and metals.
- Thermal interaction of Butyl with carbon black improves properties such as abrasion and resilience.
- Non-staining grades of Enjay Butyl do not fade or discolor on exposure to light or weather.
- Moldings and extrusions do not crack from sunlight or weather exposure and they retain new appearance and performance longer.
- Has excellent electrical properties plus resistance to ozone, corona, moisture absorption and abrasion, that is outstanding.
- Resists both heat and aging in high voltage insulation compounds.
- Low cost . . . immediate availability.

Get *all* the facts by writing or calling the Enjay Company. Complete laboratory and testing facilities are at your service.

ENJAY *Pioneer in Petrochemicals*

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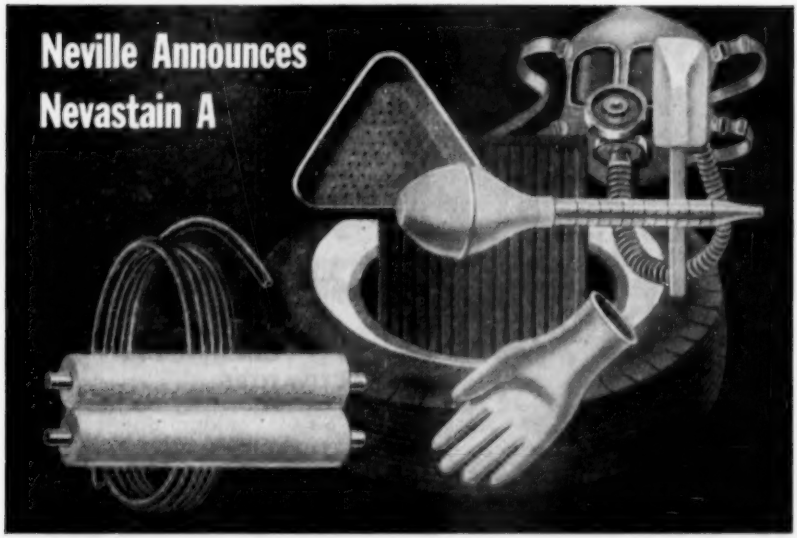

A New Non-Staining Rubber Antioxidant with Superior Characteristics

Nevastain A is an excellent non-staining, non-discoloring antioxidant with very low volatility and good stability. Synthetic and natural rubber compounds using Nevastain A have superior physical characteristics over those containing competitive non-staining antioxidants. Among its virtues are that it does not retard vulcanization, does not have an accelerating effect and does not bloom uncured or cured stock when used in normal quantities. This new product is being produced on a plant scale and is readily available and attractively priced. Use the coupon below to write for Technical Service Report No. 45.

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Resins — Coumarone-Indene, Heat Reactive, Phenol Modified Coumarone-Indene, Petroleum, Alkylated Phenol • **Oils**—Shingle Stain, Neutral, Plasticizing, Rubber Reclaiming • **Solvents**—2-50 W Hi-Flash, Wire Enamel Thinners.

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BEUTENE* HEPTEEN BASE*
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Reclaimed Rubber
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Write, on your letterhead, for technical data or assistance with any Naugatuck product.

†these products furnished either in powder form or fast-dispersing, free-flowing NAUGETS.

Naugatuck Chemical
Division of United States Rubber Company
Naugatuck, Connecticut

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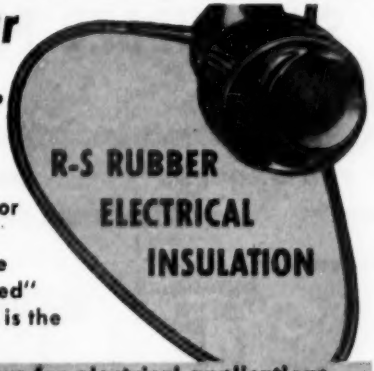

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GRADE	CLASS	END USES
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NAUGAPOL 1018	Non-staining	Crosslinked processing aid. Wire and cable and mechanical goods.
NAUGAPOL 1019	Non-staining	Standard grade for wire and cable and mechanical goods.
NAUGAPOL 1023	Staining	Low styrene content. Wire and cable and mechanical goods for arctic service.

COLD TYPES

GRADE	CLASS	END USES
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NAUGAPOL 1504	Non-staining	Low styrene content. Wire and cable and mechanical goods for arctic service.

For technical data, information or assistance that will help you in processing of your rubber compounds, write to us on your company letterhead.

Naugatuck Chemical

Division of United States Rubber Company
Naugatuck, Connecticut

IN CANADA: NAUGATUCK CHEMICALS, Elmira, Ontario • Cable Address: Rubexport, N. Y.
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IF YOU PROCESS	USE	BECAUSE
OIL EXTENDED POLYMERS GR-S TYPES 1703 1707 1708 1801	CIRCOSOL-2XH	New low cost! Low staining properties on white goods. Improves GR-S rebound. Constant uniformity assures minimum downgrading.
OIL EXTENDED POLYMERS GR-S TYPES 1705 1709 1710	SUNDEX-53	Versatile. Highly compatible with natural rubber, reclaims, GR-S types.
NEOPRENE WHV	SUNDEX-53	Cost of compounds comparable to low-cost elastomers.
REGULAR NEOPRENES and NATURAL RUBBER	CIRCO LIGHT RUBBER PROCESS-AID	True softening by physical changes in rubber structure. Large quantities absorbed without blooming.

To learn more about using Sun Rubber Process Aids to get better physicals, lower costs, and easier processing, see your Sun representative. Or write for your copy of Sun's latest Technical Bulletin describing any of the above products. Address SUN OIL COMPANY, Philadelphia 3, Pa., Dept. RC-4.

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PHILADELPHIA 3, PA.

IN CANADA: SUN OIL COMPANY, LTD., TORONTO AND MONTREAL

APRIL - JUNE • 1956

VOLUME XXIX • NUMBER TWO

RUBBER CHEMISTRY AND TECHNOLOGY

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Rubber Chemistry and Technology is published quarterly under the supervision of the Editor, representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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FUTURE MEETINGS

Meeting		City	Hotel	Date
1956	Spring	Cleveland	Cleveland	May 16–18
1956	Fall	Atlantic City	Chalfonte-Haddon Hall	September 19–21
1957	Spring*	Montreal	Sheraton-Mt. Royal	May 15–17
1957	Fall	New York	Commodore	September 11–13
1958	Spring	Cincinnati	Netherlands Plaza	May 14–16
1958	Fall	Chicago	Sherman	September 10–12
1959	Spring	Buffalo	Statler	May 13–15
1959	Fall	Atlantic City	**	September 16–18

* Joint meeting with the Rubber Division of the Canadian Institute of Chemistry.
** Hotel not yet assigned by the American Chemical Society.

GEORGE OENSLAGER (1873–1956)

George Oenslager was a member of a class of scientists that is gradually passing away, consisting of those rare folk who plan and perform on an individual rather than on a group basis. By training and performance George Oenslager was an individualist. He always wished to determine for himself exactly what the problem was, and how important it was to solve it. His solution was usually along unconventional yet commercially profitable lines.

But in spite of his individualism, he continually worked for his fellow men to raise moral standards, to improve working conditions, and to maintain the highest professional standards.

He lived and worked in a period when the managements of the rubber companies felt that important developments must be maintained as trade secrets; hence there are few patents or publications to show his contributions to the industry.

George Oenslager was born in Harrisburg, Pennsylvania on September 25, 1873. He studied at Harvard under the great analyst and atomic weight scientist, T. W. Richards, and it was there that he developed his appreciation and technique for analytical chemistry. He always felt that accurate analysis was half the solution of a problem and perhaps for this reason he persisted throughout his life in doing his own analytical work rather than entrusting it to others. He received the A.B. degree in 1894, but had such confidence in the future of chemistry that he stayed on as an instructor for two years, during which time he earned his A.M. degree.

From Harvard he went to Rumford, Maine, where he worked as a chemist in the paper factory of S. D. Warren and Company. When given the problem of improving the bleaching of paper, he concluded that the greatest immediate need was to find a cheap method for obtaining hypochlorite. The problem was one of shipping chlorine. Neither tank cars nor large pressure cylinders were available for this purpose at that time. In his typical practical manner he developed a method for preparing a highly concentrated, stable calcium hypochlorite solution and then, since he found that iron surfaces catalyzed the de-

composition of hypochlorite, he developed a coating which was applied to the interior of tank cars so the hypochlorite could be shipped without loss from its point of manufacture to the paper mill.

Oenslager's outlook on research and industry was profoundly influenced by a visit to the laboratories and factories of the I. G. Farbenindustrie in Germany at about the turn of the century. He often spoke of the importance of organized support for individual research. From a later visit in 1938 he returned convinced of the importance of developing a synthetic rubber industry in U.S.A.

In May, 1905 George Oenslager came to Akron to work for the Diamond Rubber Company. Arthur H. Marks, factory manager of the company, who had devised a solvent process for removing the resin from low grade rubber, assigned to him the problem of finding the ingredient which enabled high grade Brazilian rubber to vulcanize so much more rapidly and to have higher tensile strength than that of African rubbers or extracted rubbers. Mr. Marks expected the natural ingredient to be isolated and synthesized. Oenslager felt that a simpler way of tackling the problem would be to try the effect of adding small quantities of all sorts of chemicals to the extracted rubbers. He decided to start with inorganic compounds representative of each group of the periodic table. Charles Goodyear had previously found that litharge, magnesium oxide, and calcium oxide had accelerating activity, but none of these compounds was sufficiently active to effect the vulcanization of Marks' extracted rubbers. Oenslager now found that mercuric iodide when added in small proportions speeded up the vulcanization of extracted rubber and imparted as high tensile strength as that of Brazilian rubber. Tires were made and tested. When first made, they gave good performance, but the rubber perished so rapidly that the process was commercially valueless.

Oenslager next felt that he must try representatives of each class of organic compounds. One of the first he tried in 1906 was aniline, as representative of amines. This he found to be an accelerator which also prevented perishing of the rubber. Again tires were made and tested. These gave excellent performance and did not deteriorate appreciably under usual storage conditions. However, aniline was dangerous because of its toxicity. He then discovered thiocarbanilide, a derivative of aniline, to be highly effective and much less poisonous. Actually, aniline continued to be used in the rubber for coating the cords but thiocarbanilide was used in the treads. Oenslager developed the commercial process for making thiocarbanilide, and production was expanded until the plant was producing over 2,000,000 pounds per year. When at the beginning of World War I, aniline could no longer be purchased, he helped design the plant that was built for producing the aniline required. This was one of the first aniline plants to be established in the United States.

Soon after his employment by the Diamond Rubber Company, George Oenslager introduced numerous improvements in the process for extracting resin from the low grade rubbers. Of particular importance was his method for recovering acetone vapors by scrubbing the air from the drier with water and then recovering the acetone by scrubbing with heavy hydrocarbon oil. This solvent recovery process was the forerunner of the process for extracting casing head gasoline from natural gas.

In his early work George Oenslager found *p*-nitrosodimethylaniline to be a superior accelerator; however, rubber containing it stained everything yellow. David Spence, working independently at B. F. Goodrich, found that a modified derivative, namely *p*-aminodimethylaniline, had much less staining effect.

After the merger of Diamond Rubber Company with B. F. Goodrich in 1912, Oenslager developed a commercial method for producing *p*-aminodimethylaniline. This was incorporated into the rubber by soaking crude rubber sheets in an aqueous solution of the amine. After a period of drying and oxidation, this rubber had outstanding vulcanizing and aging characteristics. This was the famous No. 11 Rubber of the industry.

When Oenslager heard of the work at Silvertown in England, he appreciated at once the importance of the British discovery of the use of carbon black in rubber compounds. He is credited with the development of the process of compounding large proportions of carbon black in tread stocks to improve abrasive resistance.

In 1920, he went to Japan as technical advisor to the Yokohama Rubber Company, where he had an opportunity to try personally on a commercial scale many of his ideas on organic accelerators. There he also gained a high appreciation for Japanese culture and art.

He returned to the U.S.A. by way of the East Indies, where he spent several months studying rubber production on the plantations. He worked intensively to reduce the variability of crude rubber. While he did not succeed, he found that a small amount of zinc sulfate in the acetic acid used for the coagulation of latex gave a rubber which did not putrify during drying and shipment.

On his return to Akron he resumed work in the research laboratories of the B. F. Goodrich Company, where he developed a process for safely removing solvent from cord or fabric which had been treated with rubber cement. The principle involved in the process was to keep the solvent concentration in the air above the upper explosive limit.

Oenslager was much interested in the fact that vulcanized rubber articles can be converted to tough strong hydrochloride by treating them with a mixture of ethyl acetate and hydrogen chloride. He felt that by proper utilization of this and similar chemical information it might be possible to produce tires without the use of fabric.

He maintained an interest in protective coatings and tank linings. He found that rubber reacts with sulfur dioxide in the presence of traces of oxygen to give a durable resistant coating. Further, by the use of ultra-accelerators it was possible to prepare a hard rubber compound that would cure in boiling water, provided that the surface was covered with a metal foil or impervious rubber stock to reduce leaching of the accelerator during cure. This compound was widely used in rubber linings designed for boiling water cure in the field.

Oenslager continued to work on many ideas he had gained in Japan. He tried finishing rubber articles with the latex used by the Japanese for making their famous lacquer ware. He developed thermoplastic molds for plaster casting, composed of polyvinyl chloride, plasticizer, and Japan wax.

All through his life he was in love with his profession, but it was not until 1939 that he added another love and married Ruth Alderfer shortly before his retirement.

He continued to work in a laboratory which he equipped in the basement of his home in Fairlawn. He also became interested in farming and dairying and purchased a farm in Sharon Center, where he had one of the best producing herds of Jerseys in Northern Ohio.

Oenslager received the highest professional honors for his scientific contributions. He was awarded the Perkins Medal in 1933 and the Charles Goodyear Medal in 1948. He was granted the honorary degree of Doctor of Science by

the University of Akron in 1939. He became a member of the American Chemical Society in 1910 and of the American Institute of Chemical Engineers in 1916; he became a Fellow of the Institution of the Rubber Industry of Great Britain in 1936. He also was chairman of the Akron Section of the American Chemical Society.

Aside from his profession, Oenslager had a wide interest in business, charities, art, and travel. During his later years, he and Mrs. Oenslager traveled in Mexico, Guatemala, and South America, studying early Indian science and art. He made an outstanding collection of typical items of art, and took many colored photographs of the countries he visited.

He and Mrs. Oenslager had a great appreciation of the culture and art of Spain, France, Italy, and Greece. In the winter of 1955–56 they planned another trip to the Mediterranean countries. While in New York visiting his friend, David Spence, he noticed some bronchial difficulty. He decided to proceed with the projected trip since he felt he would be as well off on shipboard as anywhere else. But complications developed, and he died on board ship February 5, 1956.

His body was sealed in a lead-lined Portugese casket of inlaid wood and flown back to Akron. There his friends and professional associates laid to rest this pioneer of the rubber industry.

W. L. SEMON

George Oenslager—Biography

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See also: "American Men of Science", "Who's Who in America".

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Patents by George Oenslager

U. S. Patent 1,513,928, November 4, 1925. Recovering solvent from cord treated with rubber cement.
U. S. Patent 1,841,295, January 12, 1932. Converting surface of rubber articles to hydrochloride.
U. S. Patent 1,925,879, September 5, 1933. Treating rubber sheet or films with sulfur dioxide.
U. S. Patent 2,048,808, July 28, 1936. Method for making a resilient gel of polyvinyl chloride for use as a mold for plaster castings.
Brit. Patent 367,305, January 19, 1931. Method for producing ebonite by vulcanization of a rubber compound in boiling water.

NEW BOOKS AND OTHER PUBLICATIONS

PROCEEDINGS OF THE THIRD RUBBER TECHNOLOGY CONFERENCE: 1954. Edited by T. H. Messenger. Published by W. Heffer & Sons, Ltd., Cambridge, England. Available in the United States from *Rubber Age* 101 W. 31st St., New York 1, N. Y. $7\frac{1}{4} \times 9\frac{3}{4}$ in. 844 pp. $13.50.—The Third Rubber Technology Conference, under the auspices of the Institution of the Rubber Industry, was held in London, June 22–25, 1954. Fifty papers were presented, all of which are in this volume. The conference maintained its international character, 19 countries being represented and 784 members registering, an increase

of 120 over the 1948 attendance. That the conference was a success is shown by the fact that, since its close, the Institution has decided to hold a Fourth Conference in 1959 and to give it the necessary financial support.

In this Third Conference the study of fundamentals was notable. Molecular structure, physical structure, high-polymer chemistry, the nature of chemical reactions in rubber, and the nature of reinforcement figured prominently. The titles and authors are the following.

Properties of natural-rubber latex: **Microgel in Latex and Sheet Rubber,** by R. Freeman; **Improved Rubbers by the Enzymatic Deproteinization of Skim Latex,** by J. E. Morris; **Stability of Ammoniated Latex and Soap-Stabilized Emulsions in the Presence of Complex Zinc Salts,** by T. S. McRoberts; **Variability of Hevea Latex,** by W. L. Resing; **Zinc Oxide Testing of Latex,** by E. W. Madge, H. M. Collier, and J. L. M. Newnham; **Hevea Latex: Its Structure and Viscosity,** by G. Verhaar; **Contribution to the Study of Mineral Elements in Field Latex,** by E. R. Beaufils; **Rubber Peptized on the Plantation,** by G. Giger, J. Lemee, and M. Liponski.

Production and evaluation of synthetic rubber: **Cation and Anion Influence in the Alfin Reagent for the Polymerization of Butadiene,** by A. A. Morton, I. Nelidow, and E. Schoenberg; **Evaluation of Synthetic Rubbers and Latexes,** by I. D. Patterson; **Recent Studies on the Structure of Synthetic Rubber,** by R. F. Dunbrook, B. L. Johnson, J. L. Binder, J. M. Willis, and E. L. Carr; **Rubbery Copolymers from Unsaturated Ketones,** by W. Cooper, T. B. Bird, and E. Catterall; **Preparation and Properties of Condensation Block Copolymers,** by D. H. Coffey and T. J. Meyrick; **Graft Polymers Derived from Natural Rubber,** by G. F. Bloomfield, F. M. Merrett, F. J. Popham, and P. McL. Swift; **Oil Resistance of Synthetic Rubbers Over Very Long Periods of Time** by B. Sarno; **Structure and Solution Properties of High Molecular-Weight Butadiene-Styrene Copolymers,** by R. B. MacFarlane and L. A. McLeod; **Pyridinium High Polymers,** by W. B. Reynolds, J. E. Pritchard, M. H. Opheim, and G. Kraus.

Chemistry of rubber: **Studies in Latex Particle Reactions: Kinetics of Hydrochlorination of Unvulcanized and Vulcanized Latexes,** by M. Gordon and J. S. Taylor; **Oxygen-Absorption Effects in Cured and Uncured Natural Rubber,** by R. L. Stafford; **Infrared Spectroscopic Analysis of Elastomers,** by W. H. T. Davison and G. R. Bates; **Structural Characteristics of the Sulfur Linkage in Natural-Rubber Vulcanizates,** by L. C. Bateman, R. W. Glazebrook, C. G. Moore, and R. W. Saville; **Chemical Reactions of Antioxidants Used in Vulcanized Rubber,** by P. Schneider; **Cross-Linking and Radiation Effects in Some Natural and Synthetic Rubbers,** by A. Charlesby and D. Groves.

Physics of rubber: **Modification of the Permeability of Natural-Rubber Vulcanizates,** by P. Thirion; **Reinforcement and Tear Strength Anisotropy,** by H. J. J. Janssen; **Elasticity of Ideal and Real Rubberlike Materials,** by H. M. James and E. Guth; **Study of Rubberlike Polymers by Nuclear Magnetism,** by B. A. Mrowca and E. Guth; **Natural-Rubber Compounds for Intermittent Low-Temperature Service,** by W. P. Fletcher, A. N. Gent, and R. I. Wood; **Theoretical Model for the Elastic Behavior of Filler-Reinforced Vulcanized Rubbers,** by L. Mullins and N. R. Tobin; **Nonlinearity in the Dynamic Properties of Rubber,** by A. R. Payne.

Developments in testing methods: **Tear-Down Adhesion Testing,** by B. Pickup; **"Constant-Power Principle in Abrasion Testing,** by E. F. Powell and S. W. Gough; **Changes of Electrical Resistance of Rubbers Loaded with Carbon**

Black, by D. G. Marshall; **Tire-Cord Fatigue and Fatigue Testing,** by R. S. Goy; **Pneumatic Tire Testing,** by J. I. S. Williams and R. G. Clifton; **Fast Easy Test for Measuring Relative State of Cure,** by L. R. Sperberg.

Compounding: theory and practice: **Nature of Chemisorptive Mechanisms in Rubber Reinforcement,** by V. A. Garten and G. K. Sutherland; **Interaction of Rubber and Fillers During Cold Milling,** by W. F. Watson; **Role of Intermediate Level Carbon Blacks in Rubber,** by I. Drogin; **Role of Particle Diameter and Linkage Formation in Rubber Reinforcement,** by A. F. Blanchard; **Lignin as a Compouding Ingredient for Natural Rubber,** by I. Sagajllo; **Mooney Viscosity of Carbon Black-Rubber Mixtures,** by M. Studebaker; **Oil Extension of Natural Rubber,** by G. J. van Amerongen and H. C. J. de Decker; **Behavior of Highly-Filled Rubber Vulcanizates,** by K. C. Gryant and D. C. Bissett; **Rubber Reinforcement by Resins Formed in Latex,** by J. van Alphen.

Miscellaneous technology: **Abraded Filament Tire Cord,** by E. R. Gardner, A. E. Herbert, and W. C. Wake; **Effect of Heat Setting on the Physical Properties of Terylene Polyester Fiber,** by D. N. Marvin and T. J. Meyrick; **Time-Dependent Effects in Tire Cords,** by J. O. Wood and W. F. Kilby; **Wave Phenomena in Tires at High Speed,** by D. M. Turner; **Tread Wear and Fuel Consumption of Tires,** by H. C. J. de Decker, R. Houwink, and G. J. van Amerongen.

The volume includes author and subject indexes and reference to various social functions. Exhibits at the conference are classified and arranged in twelve groups. The organizations responsible for the development and manufacture of the instruments are indicated. Where instruments have been described in patents or in the literature, some references are given. [From the *Rubber Age* of New York.]

Classes and Properties of Compounding Materials for Use in Elastomers. By I. Drogin. United Carbon Co., Inc., Charleston 27, West Va. 8½ × 11 in. 48 pp.—This is a reprint of a lecture by Dr. Drogin at the New York Rubber Group's Elastomer Technology Course. It classifies the more important available compounding materials and describes their properties and functions. Using tables to group the materials, the author discusses the composition of a rubber compound relative to the selection of elastomer, peptizer, vulcanizing agent, accelerator, filler, and plasticizer. The many grades of carbon blacks are grouped under 16 types according to particle fineness, electrical conductivity, processing, and extrusion, and reinforcement as exemplified by stress-strain and resistance to abrasion. In addition, the author also discusses organic nonblack reinforcing materials, organic loading materials, extenders, diluents, softeners, processing aids, plasticizers, protective materials, and miscellaneous groups of compounding materials. [From the *Rubber Age* of New York.]

Some Aspects of the Crystallization of High Polymers. By G. Schuur, Member of the Staff of the Rubber-Stichting. Rubber-Stichting, Oostsingel 178, Delft, The Netherlands. 1955. 82 pp. 15.5 × 24 cm. Price, Five Dutch florins.—This short book (82 pages) is essentially a review of certain aspects of crystallization phenomena in high polymeric systems. The five chapters are concerned with: a general introduction; formation, structure, and melting of spherulites; mechanism of crystallization; continuity of the crystal lattice, particularly in oriented and stretched polymers; rate phenomena

and the melting range. The author refers frequently to papers published up to and including 1954, making this booklet up to date.

In addition to a discussion of the published work on those topics selected, this book contains an appreciable amount of original material by the author. It is well organized and written. This reviewer was particularly taken by the beautiful microphotographs of spherulites taken with polarized light. The diagrams showing the growth of these spherulites are unusually clear.

This book is recommended to the attention of those interested in the crystal properties of high polymers. It is not at all complete, since the author addressed himself only to "some aspects", particularly those dealing with natural-rubber systems. For example, there is no detailed discussion of the excellent recent work on crystalline high polymers. Therefore, within the limits which the author has set for himself, he has done an excellent job. [From the *Journal of the American Chemical Society.*]

RUBBER RED BOOK. 1955–56 Edition. *Rubber Age*, New York, N. Y. Cloth cover, 6 × 9 inches, 1249 pages. Price, $10.—This tenth edition of the Red Book supplies data on 1410 rubber manufacturers in the United States and Canada, giving concise information on executive personnel and types of products manufactured. Sections listing manufacturers of equipment, accessories, compounding materials, textiles, among others, are, as usual, included. Special sections are devoted to natural, synthetic, reclaimed, scrap, and latex rubber. The "Who's Who" is again a valuable feature. Other sections include information on sales and export agents, educational courses planned or being given, trade and technical organizations, and technical journals. [From the *Rubber World.*]

PROGRESS REPORT ON THE COOPERATIVE HEVEA RUBBER DEVELOPMENT PROGRAM IN LATIN AMERICA. By R. D. Rands and Loren G. Polhamus. (Circular No. 976). U. S. Department of Agriculture, Washington, D. C. 6 × 9 in. 84 pp. 35c. (Prints available from the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C.)—This circular presents a 14-year summary of major activities and results from the cooperative research and development program designed to establish a rubber-producing industry in nine Latin-American republics—Bolivia, Brazil, Colombia, Costa Rica, Dominican Republic, Guatemala, Haiti, Mexico, and Peru. The United States objective is to create a "living" stockpile within the U. S. defense zone that may eventually reduce or eliminate the government's costly strategic stockpile of Far Eastern rubber stored within the country. Latin American objectives, according to the circular, are principally (1) self-sufficiency of rubber for internal consumption, and (2) to grow rubber as a cash crop on the undeveloped lowlands by colonists and settlers from the overcrowded highlands. The United States Department of Agriculture participation has consisted in the establishment and maintenance of regional field stations in Costa Rica, Guatemala, and Haiti, respectively, for basic research, breeding, and disease resistance testing, and assignment of specialists and experienced development advisers to cooperate with local scientists in the other six countries. [From the *Rubber Age* of New York.]

PRÜF-, MESS-, UND KONTROLL-GERÄTE-LEXIKON, 1954. Edited and compiled by Hans Hadert. First Edition. Published by Hadert-Lexikon-Verlag,

Martin Luther Strasse 88, Berlin W. 30, Germany. Board covers, $8\frac{1}{4} \times 6$ inches, 750 pages. Price D. M. 38.00, plus postage and packing.—Numerous inquiries over a long period of years, the editor says in his foreword, revealed that even in large factories there was often complete ignorance about many serviceable testing, measuring, and checking instruments. At the same time came frequent requests for a reference book giving helpful information about types of devices required to solve specific manufacturing problems. Since no such work has hitherto been available, either in Germany or abroad, Hadert undertook to fill this lack, and now presents the 1954 lexicon of testing, measuring, and recording instruments, the first of its kind, it is claimed.

In 96 sections, including several hundred illustrations, all kinds of modern German and foreign devices for the most varied purposes are described, and many of the chapters have bibliographies that should prove valuable to those wishing to go deeper into the problems. Rubber and plastics manufacturers will find devices for checking, determining or testing redox values, elasticity, porosity, melting, softening and flow points, abrasion, aging, flash and ignition points, effects of climate, dimensional stability, permeability, also x-ray, ultrasonic, dialysis, and ultrafiltration equipment. [From the *Rubber World.*]

Instruments for Measurement and Control. Werner G. Holzbock. Reinhold Publishing Corp., 430 Park Ave., New York 22, N. Y. Cloth, 6×9 inches, 376 pages. Price, $10.00.—This book describes and illustrates all the more recent devices to measure and control temperature, moisture, pressure, flow, liquid level, density, viscosity, and speed. Written in non-mathematical language, it is intended as a reference work on instrumentation and quality control.

Eight chapters are devoted to the instruments mentioned above; other chapters cover material specification analysis, automatic controller action, electric controllers, self-operated controllers, time function controllers, and final-control elements. A special chapter discusses the development of centralized systems, miniaturization, and digital computers.

Schematic reproductions of all types of instruments are included.

Technicians not directly concerned with instrumentation should find this book useful as a review of physical elements. [From the *Rubber World.*]

ABRASION OF BUTYL RUBBER *

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In relation to the vast quantity of literature on the physical properties of rubberlike materials, the amount of published work on the abrasion of rubber is quite small. This situation is surprising in view of the fact that abrasion resistance is of prime importance to the large volume use of rubber. Perhaps it is because so much of the work in this field has been directed toward the prediction of service wear rather than an understanding of the factors involved in the abrasion of highly elastic materials. The consensus of most of the work in abrasion has been that laboratory tests at best are only a rough indication of how a rubber vulcanizate will perform in service. Service wear tests provided the final answer.

It is possible that too much was expected of laboratory abrasion tests before rubber abrasion was understood. It was felt at the inception of this present study with Butyl rubber that a further understanding of the factors involved in abrasion would eventually aid in obtaining better road wear correlation. Thus the two purposes of understanding abrasion and predicting service wear would be welded into a single objective. A better understanding of abrasion could also aid the development of a tire from a new polymer such as Butyl. It would direct the molecular and compounding changes necessary for improved wear resistance.

THE LAMBOURN ABRADER

To start our study of abrasion, the Lambourn abrader was selected as the laboratory instrument. Developed at Dunlop Tire & Rubber Co. in England, it has not been widely used in this country. Two recent articles[1] are among the few publications of abrasion studies made with this machine.

This type of abrader was selected because variations of velocity of slip and braking force can be made. An indication of braking force is important. It was pointed out more than 25 years ago by Williams[2] that work done on the sample should be related to volume loss of rubber. This relation, of course, would be valid at a given velocity of slip.

DESCRIPTION OF THE ABRADER

The Lambourn abrader simulates the rolling deformation of a rear wheel under load. In this case a small disk of rubber is driven against an abrasive wheel. A variable-speed electric motor drives the sample wheel at a prescribed rpm, and it in turn rotates the abrasive wheel. Attached to the shaft of the abrasive wheel is a metal disk which operates in a variable magnetic field and thus supplies a variable degree of resistance to rotation. This varying degree

* Reprinted from the *Rubber World*, Vol. 133, No. 1, pages 59–68 and 76–77, October 1955. This paper was presented before the Akron Polymer Lecture Group, Akron, Ohio, November 5, 1954, and before the Division of Rubber Chemistry of the American Chemical Society at its meeting in Detroit, Michigan, May 4–6, 1955.

of resistance causes a change in the degree or velocity of slip between the sample wheel and the abrasive wheel.

A schematic sketch in Figure 1 shows the rudiments of the machine. The degree of slip is positively determined by two revolution counters attached to the sample wheel and the abrasive wheel shafts. The tachometers serve as a guide so that slip may be controlled during the course of the experiment. With the rubber disk rotating at a prescribed 600 rpm, various abrasive wheel speeds can be controlled by the current to the magnetic brake, producing the different degrees of slip. Slip can be varied from 5 per cent to about a maximum of 40 per cent, depending on the amount of electrical current supplied to the coils of the brake. The variations in current requirement are recorded on a chart so that an average for the entire run can be calculated. Since the apparatus is supplied with a constant d.c. voltage, amperage measurements are directly related to power or electrical energy supplied to the brake.

Based on the relative dimensions of a sample wheel and a regular tire tread, a seven-pound load on the sample would produce about the same unit area load

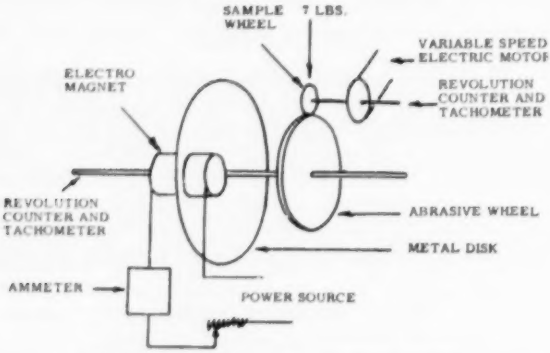

FIG. 1.—Schematic drawing of Lambourn abrader.

as that borne by a commercial tire. A standard-size tire and wheel revolve in the neighborhood of 600 rpm at 60 miles per hour. Although these conditions have been varied during the laboratory study of abrasion, a 600-rpm sample speed and seven-pound load have been designated as standard.

TYPE OF DATA OBTAINED

Under the standard conditions of wheel load and sample speed, variations of the amount of slip are obtained by changing the electric current of the magnetic brake. The effect of this change on the abrasion of a Butyl-channel black tread is shown in Figure 2. Plotted on rectangular coordinates, one curve (solid line) relates the degree of slip to the abrasion loss, and the other curve (broken line) shows the braking force, in terms of amperes to the brake, required for a given degree of slip.

Figure 2 graphically shows how sensitive is abrasion loss to the degree of slip, and thus it is not surprising how conditions of driving will greatly alter tire life on the road. The curve appears exponential in character. The reading of current to the magnetic brake, at constant d.c. voltage, will be that fraction of

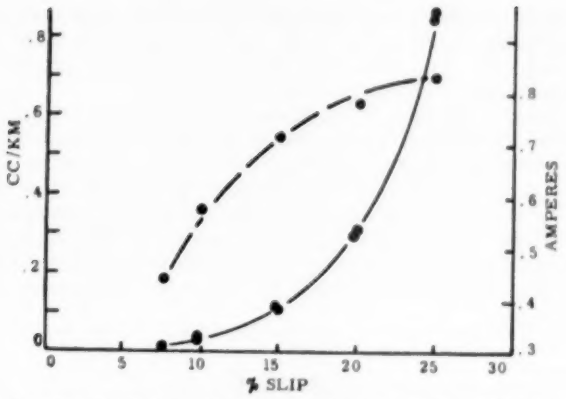

FIG. 2.—Abrasion loss and amperes of the brake vs. % slip. Solid line, cc./km. Broken line, amperes.

the original energy input at the motor after mechanical friction and heat build-up in the rubber have been substracted. As such, then, it will be a measure of the resistance to slippage between the abrasive wheel and the rubber surface. This resistance is made up of interfacial tension and the energy of abrasion. Since sliding friction is always accompanied by some degree of abrasion[3], the resistance, in this instance, will be considered frictional under severe conditions of abrasion.

Support for this combination of factors, as applied to rubber abrasion, is found in the classical observations on sliding friction[4]. These experiments have shown that the sliding friction between two surfaces is related to the logarithm of the velocity of slip. Since the sample wheel is running at constant speed, an increase in the percentage slip is the same as an increase of the velocity of slip. On this basis, then, a measure of the electrical current requirements for a given degree of slip is an indication of friction, as shown in Figure 3.

The exponential character of the relation of degree of slip and abrasion loss is displayed also in Figure 4 where the variables form a linear plot on logarithmic coordinates. The slope of the line is approximately four; in fact, a large number of plots during the course of this study yielded slopes between about 3.7

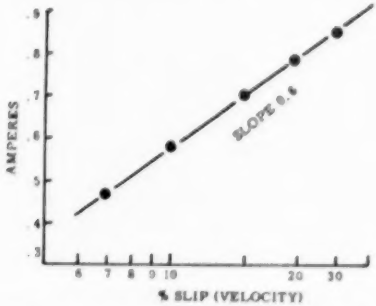

FIG. 3.—Amperes vs. % slip may also be termed friction vs. velocity of slippage.

and 4.3. It has, therefore, been stated in a generalized form that the abrasion loss is related to the fourth power of the degree of slip. Abrasion experiments conducted at a given slip, wherein small experimental variations occur, have been corrected to the exact degree of slip on this basis.

A cross plot of the data of Figure 2 relates abrasion loss as a function of the electrical current to the brake. The points are best fitted by a semilogarithmic plot. Why abrasion loss should increase so drastically with either degree of slip or electrical current to the brake is unexplained at this time. One could postulate on the basis of rate of energy input that abrasion loss should be directly related to velocity of slippage. Although insufficient data are available, the effect might be attributed to a surface temperature increase as velocity of slip is increased. Thus abrasion loss would appear as an accelerating function of degree of slip.

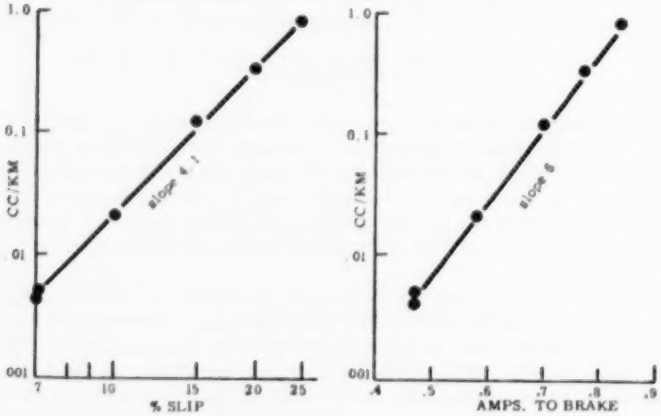

FIG. 4.—Relation of abrasion loss to slip and braking force.

THE ABRASION OF GR–S AND BUTYL TREAD COMPOUNDS

When abrasion experiments were first conducted with different types of rubbers, relations between degree of slip and abrasion loss were frequently not the same. In Figure 5 the behaviors of a Butyl tread and a GR-S tread are shown. Each tread contains 50 parts, per 100 of rubber, of an MPC channel black. The GR-S compound is vulcanized with 1.7 parts of sulfur and one part of Santocure[4] in a conventional formulation. The striking feature of this logarithmic plot is the crossing of the lines. For these two compounds this figure indicates that the Butyl tread is superior at lower degrees of slip, and the GR-S tread at higher degrees of slip. Such a behavior could be explained on the grounds that Butyl has a slower relaxation time than GR-S and consequently does not adjust to higher velocities of deformation as well as GR-S. Thus at a slower degree or velocity of slip the Butyl molecules have more time to orient under surface deformation and thus present a greater resistance to rupture.

An important part of this abrasion analysis is the lower curves relating degree of slip to electrical input to the magnetic brake. The relative position of

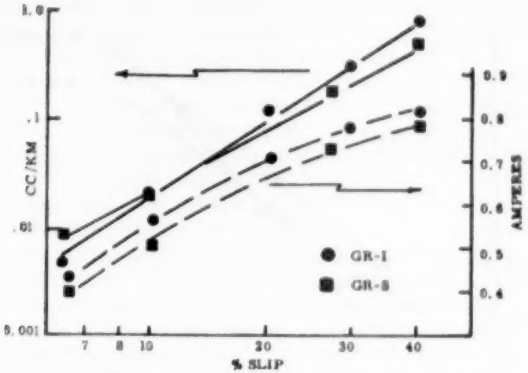

FIG. 5.—Slip vs. abrasion loss for GR-S type and GR-I (now Enjay Butyl) treads.

the two curves indicates that, to obtain a given slip, more braking force must be supplied to the Butyl compound. If abrasion loss is then based on the loss per kilometer per ampere to the brake, the plot of abrasion loss vs. slip would be lowered for Butyl in relation to the GR-S tread. Further, if abrasion loss is determined as a function of electrical energy to the brake (regardless of the degree of slip), Butyl would be everywhere superior to the GR-S.

Figure 6 presents this fact pictorially at a constant current input of 0.76 ampere. The wheel on the right, a Butyl tread, is smoother, has operated at less slip, and has shown far less abrasive wear under these conditions than the GR-S. At a constant slip of 19.3 per cent, however, where the amperage to the

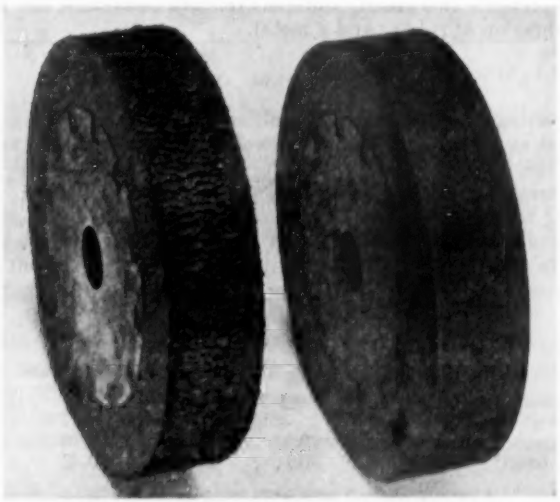

FIG. 6.—Abrasion of GR-S type and GR-I (now Enjay Butyl) at constant input of electrical current to the Lambourn abrader magnetic brake. Left: standard GR-S (MPC black), 0.76 amp. to brake, 23.8% slip, 0.67-g. loss/km. Right: GR-I-18 (MPC black), 0.76 amp. to brake, 19.3% slip, 0.28-g. loss/km.

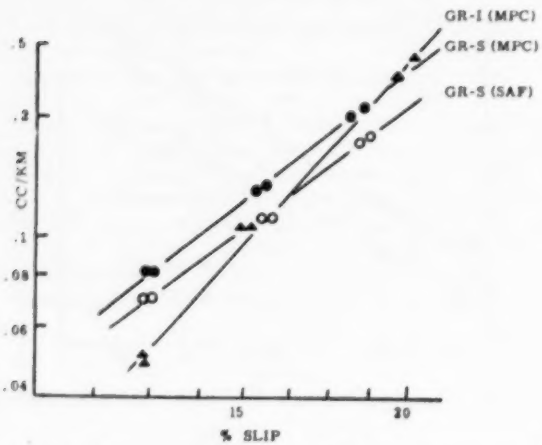

FIG. 7.—Abrasion of GR-S type and GR-I (now Enjay Butyl) tread compounds at varying % slip on Lambourn abrader.

brake is different, the GR-S compound is slightly superior to this Butyl tread. It has been suggested that this somewhat greater friction for Butyl treads is responsible for the quieter running quality of Butyl experimental tires.

This observation embracing the change of relative abrasion resistance with degree of slip has been observed in later studies. Figure 7 shows two cold rubber GR-S treads, one with a fine SAF carbon, compared to a well-prepared Butyl-channel black tread. Again the line defining the function of slip and abrasion loss crosses the lines for the two GR-S treads. An analogous observation, which presents two greatly different relative behaviors, can be made between the abrasion of rubber and a metal.

ABRASION OF STEEL AND RUBBER

An interesting example of abrasion differences of materials is given by such two extremes as rubber and steel. A steel wheel the same size as the rubber wheels was run on the Lambourn abrader and compared to a GR-I-17 (Enjay Butyl 217) tread compound. The data are presented in Table 1.

Referring to the volume loss per kilometer, the steel wheel has about one-half the loss of the rubber at 20 per cent slip, but three times the loss at 7 per cent slip. In a graph the trend would appear as shown on the left in Figure 8. At high percentage slip, steel is superior to rubber; at low percentage slip the

TABLE 1

Material	Braking Force (amp.)	% Slip	Abrasion loss		
			g./km.	cc./km.	cc./km./amp.
Steel	0.56	20.5	1.51	0.19	0.34
GR-I tread*	0.84	20.1	0.35	0.32	0.38
Steel	0.27	7.7	0.23	0.03	0.11
GR-I tread*	0.50	7.8	0.011	0.01	0.02

* Enjay Butyl.

reverse is true. In addition, the traction or coefficient of friction of rubber against abrasives is greater. Observing the electrical braking forces in the table, it is evident how much more current is required to obtain a given degree of slip for rubber, compared to steel. When braking force is taken into consideration, as shown on the right side of Figure 8, the cross-over point advances to high degrees of slip. Here abrasion loss per kilometer is adjusted to the same braking energy input, and the rubber tread appears to be even more superior to steel at low degrees or velocities of slip.

These facts illustrate why rubber has often been characterized as more resistant to abrasion than steel. For applications such as conveyor belts, coal chutes, etc., this superior abrasion resistance of rubber has been found through experience to be the case. However, if one were to grind a piece of rubber against an abrasive as an axe is ground, the reverse would surely be true. This latter condition is one of 100 per cent slip where steel is much superior to rubber. Because of the greater frictional surface of rubber belts and chutes, coal, ore, or rock particles roll and tumble along the rubber surface aided by the high elastic

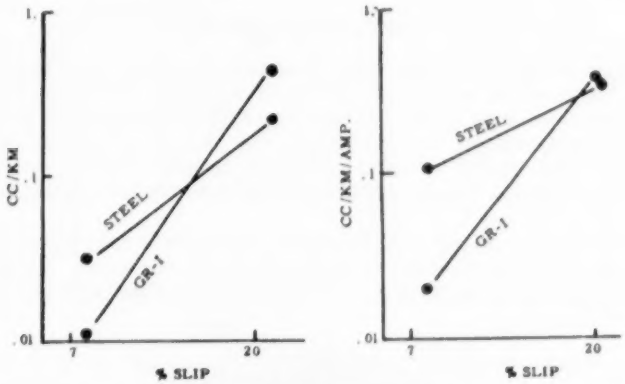

FIG. 8.—Abrasion of GR-I (now Enjay Butyl) compared to steel on Lambourn abrader.

nature of the rubber. This would be a condition of low slip where rubber is superior. On the other hand, rocks, ore, or coal on a metal chute would slide and scrape instead of rolling or tumbling, a condition of high slip resulting in higher abrasion loss, even for steel, since the absolute trend of abrasion increases with increasing velocity of slip for all materials.

PRECISION OF THE MEASUREMENTS

A discussion of the Lambourn abrader would not be complete unless some reference was made to the precision of the abrasion measurements. In general, repetitive runs, after corrections for degree of slip and braking force are made, showed a coefficient of variation of only 4.5 per cent. To illustrate this degree of precision, a sample table of six runs on the sample Butyl compound is given in Table 2.

Columns 2, 3, and 4 represent the recorded data. As corrections are made to the exact degree of slip in column 5, the standard deviation is reduced. The further refinement of column 6 adjusts the values for variations of frictional

TABLE 2

PRECISION OF ABRASION MEASUREMENTS

Butyl rubber channel black tread compound	Amp.	% Slip	cc./km.	cc./km. Cor. to 19% slip	cc./km./amp. 19% slip
A	0.71	19.1	0.219	0.215	0.302
B	0.70	19.0	0.201	0.201	0.288
C	0.67	18.8	0.168	0.175	0.264
D	0.71	19.2	0.212	0.203	0.288
E	0.69	19.0	0.192	0.192	0.278
F	0.71	18.9	0.206	0.210	0.296
	Mean		0.200	0.199	0.286
	Std. Dev.		0.018	0.014	0.013
	Coefficient of variation		9.0	7.0	4.5

factors with a further decrease of the standard deviation and coefficient of variation as a consequence.

CONDITIONS OF ABRASION

Before a more penetrating study of abrasion could be conducted, a certain amount of orientation as to proper conditions of abrasion was deemed necessary. During this orientation phase of the study, a definite anomaly was brought out between laboratory test and road wear test. In the laboratory tests with smooth surfaced wheels, a harder vulcanized compound made from a higher carbon black loading appeared slightly superior to one with lower loading of carbon black.

In controlled road tests on Butyl treads, the opposite was observed; in road tests the softer, lower loadings of carbon black were superior. Conditions of abrasion were undoubtedly different, but the tread surfaces were also different.

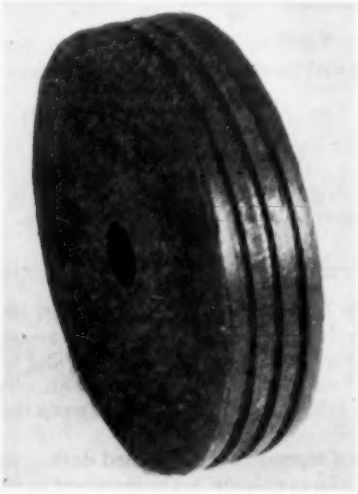

FIG. 9.—Sample wheel with four circumferential ribs for Lambourn abrader.

The actual tire had a tread pattern, and the sample wheel a smooth surface. When studies were made with a sample tread pattern on the sample wheel, unexpected observations were made.

EFFECT OF A TREAD PATTERN

A tread pattern introduces mechanical softness to the rubber surface. Each rib or other incremental surface shape may move independently of areas adjacent to it during the time the surface is in contact with the road. It is conceivable, therefore, that different slip conditions could exist and relative abrasive wear be altered.

To make observations of the effect of a tread pattern as laboratory abrasion, a sample wheel was molded with four circumferential ribs. This is shown in Figure 9. The dimensions of the wheel are $1\frac{3}{8}$ inches in diameter, $\frac{3}{8}$ inch thick, and the cross-section of the ribs are $\frac{3}{64}$ by $\frac{1}{16}$ inch deep.

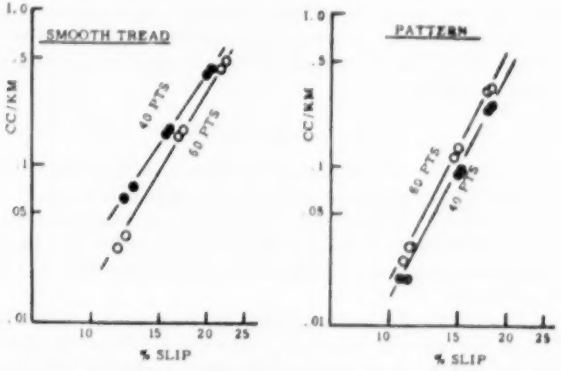

FIG. 10.—Effect of tread pattern on abrasion of Butyl compounds with two different carbon black loadings.

In Figure 10, abrasion losses are compared with a smooth wheel surface and a tread pattern, using a compound possessing 60 parts of channel black and one containing 40 parts. These abrasion losses in cc. per kilometer are compared as a function of slip for smooth treads on the left and for tread patterns on the right. The reversal of the relative positions is evident at once. In common with road wear results, laboratory abrasion losses are lower with the softer material when a tread pattern is used. A 50-part channel black compound would appear in an intermediate position. Braking force requirements are greater for the harder material in both cases, but this condition does not affect their relative positions.

Even stranger than this reversal of positions is the comparison of the absolute abrasion loss when a tread pattern and smooth surface are compared with the same compound. Such a comparison is made in Figure 11. This figure plots absolute volume loss as a function of slip. The tread pattern displays lower loss at all points in spite of the fact that actually less rubber is in contact with abrasive surface. Although not shown graphically, with very hard compounds of more than 60 parts of channel black, the advantage of the tread pattern disappears. It has been stated in a tire design publication[6] that

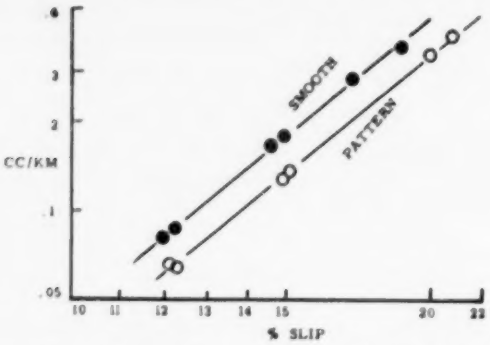

FIG. 11.—Comparison of tread pattern vs. smooth surface for the same Butyl tread compound.

a tread pattern is only used to obtain non-skid qualities, especially in wet weather. A tread pattern on an actual tire has been considered to be actually inferior to a smooth tire on the basis of road wear. These laboratory tests predict the opposite trend.

EFFECT OF WHEEL LOAD

It was indicated earlier in the discussion that a sample wheel load of seven pounds was equivalent to the unit area load of a regular tire tread. In a study of the effect of wheel load on abrasion a relation other than linear was observed. In these experiments observations were made with three Butyl treads of varying hardness. These were made from a 60, 50, and 40 parts of MPC channel black per 100 parts of Butyl.

Figure 12 gives the results of that study in two graphs. The lower portion presents abrasion loss at one degree of slip as a function of wheel load. In common with the results discussed on the effect of tread pattern, the softer tread made with 40 parts of carbon appears to an advantage at all wheel loads. An abrupt increase is noted above seven pounds, giving the curves an S shaped appearance. This irregularity appears in face of the essentially linear nature of the frictional curves in the upper portion. Here braking force requirements rise regularly with wheel load, and at all loads the harder compound requires more electrical energy.

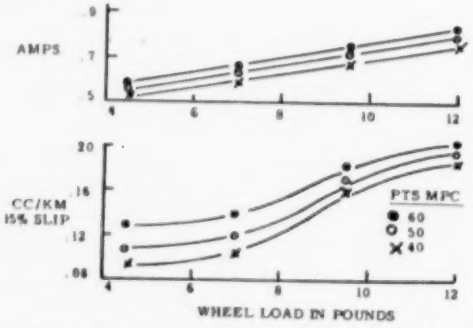

FIG. 12.—Effect of variations in wheel load on abrasion loss and braking force.

A combination of these two plots, wherein braking force is accounted for in the overall abrasion losses, brings out two interesting points, as shown in Figure 13. When abrasion loss is determined as volume loss per kilometer per ampere to the brake, the S shape of the curves becomes more pronounced. At the lower end of the load scale, the loss so calculated turns upward. In a practical sense this result can be interpreted as follows. If the load on a wheel is decreased while the same braking force is maintained, abrasion losses will increase because slippage will occur more readily. At the higher end of the wheel load scale, the convergence of the curves for the various compound hardnesses is more apparent. Thus if road tests are conducted under conditions of extreme overload, differences in mileage life or abrasion loss would tend to be made obscure.

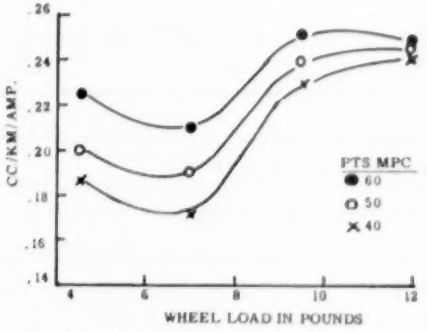

FIG. 13.—Effect of variations in wheel load on abrasion in cc./km./amp.

ABRASION AND AMBIENT TEMPERATURE

The effects of climatic temperatures have often been cited as reasons for changes in relative tire wear performance. Laboratory abrasion tests support this possibility. The Lambourn abrader had originally been equipped with a transparent plastic case which had a wide slot to accommodate the abrasive wheel. Light flexible air hose was connected to the plastic case so that air at controlled temperature could be circulated around the sample wheel. The temperature range of -20 to $+50°$ C could be obtained.

In Figure 14 the results of this experiment are presented for four different Butyl tread compounds. Curves 1 and 2 represent 50 parts of MPC channel black. No. 1 has no hydrocarbon oil plasticizer, and No. 2 has 15 parts per 100 of polymer. Curves 3 and 4 are furnace black counter-parts. No. 1 has 50 parts of an SAF carbon and no oil plasticizer; while No. 2 has 15 parts of a hydrocarbon oil. It is strikingly evident that the presence of oil makes the abrasion resistance of the tread compound more sensitive to the surrounding temperature. This point is evident with either MPC or SAF carbon, regardless of the absolute position of the curves.

In the case of the channel black, the oil-extended tread appears poorer at high temperatures and superior at lower temperatures when compared to the tread with no plasticizer. As will be discussed later, this effect probably depends on the change of elastic qualities in combination with rupture strengths of the different compounds. Such a combination of factors could also explain

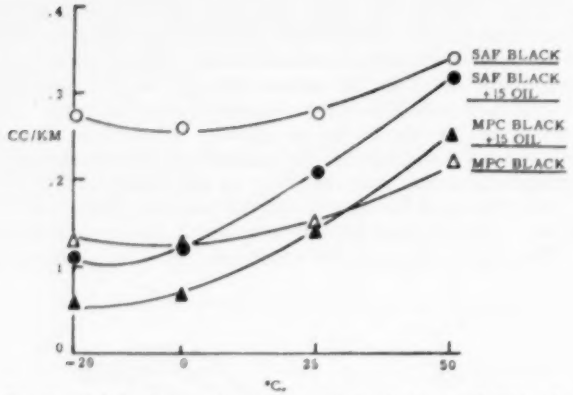

FIG. 14.—Relation between temperature and abrasion loss for Butyl treads.

the fact that the curves tend to rise as ambient temperature descends below freezing. In much the same manner, but to a much smaller extent, the abrasion of GR-S and natural rubber treads appears to be somewhat less sensitive to ambient temperature than comparable Butyl compounds.

CONCEPT OF THE ABRASION OF RUBBER

A new approach to the subject of abrasion was introduced by Schallamach[7] when he studied the abrasion of rubber by a needle. The needle was attached to a ring dynamometer which measured the thrust required to embed the needle in a revolving cylinder of rubber. The deflection of the needle indicated the tractive force or friction. Figure 15 gives a schematic sketch of the needle and the revolving rubber surface with the gouged portion of rubber ahead of the point of contact.

In the study of the needle abrasion of gum vulcanizates of natural rubber, it was observed that the tractive force decreased slightly with increasing state of cure or cross-linking, while the amount of rubber ripped off increased markedly. It would appear from these observations that the rupture strength of the rubber was decreasing rapidly with overvulcanization, as would be expected.

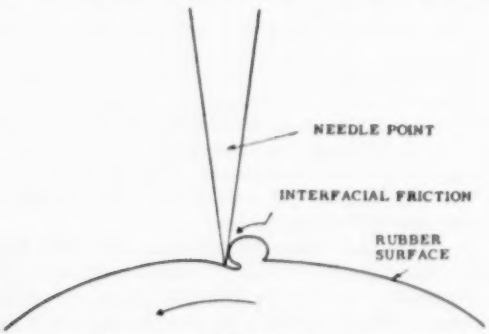

FIG. 15.—Schematic sketch of Schallamach needle abrader.

With compounds containing carbon black, tractive forces increased, but the higher modulus of the material produced gouged patterns of higher frequency. The increased rupture energy of the reinforced rubber, however, reduced the amount of ripping.

These patterns suggest that the abrasion by the Schallamach needle involves friction and rupture resistance. If the friction between the small roll of gouged rubber and the needle were sufficient and the compound strength low enough, a chunk of rubber would be ripped from the surface. Extensibility of the rubber would also be important, since the amount of work required to rupture the rubber would depend on extension. The abrasion of the rubber compound can then be postulated to be a function of the intersurface friction and the resistance to rupture.

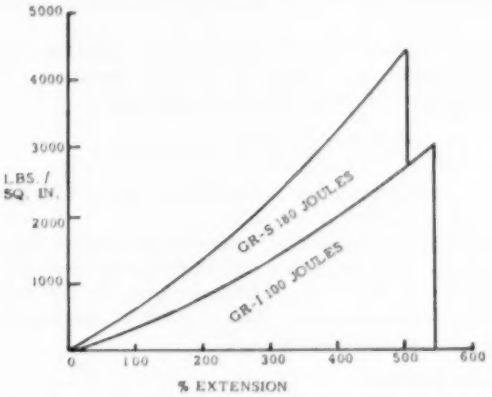

FIG. 16.—Rupture energy of typical GR-S (cold or LTP type) and GR-I (now Enjay Butyl) treads.

DEVELOPMENT FROM SCHALLAMACH

During our first experiments with Butyl rubber abrasion and also with tire wear, it was puzzling that Butyl should give as great as, and sometimes greater resistance to abrasion than, a compounded, 41° F GR-S. The GR-S compound would always have a greater energy of rupture than the best GR-I compound that could be made. This point is illustrated in Figure 16, where the energy or work of rupture is depicted by the area under the stress-strain curves. A representative GR-S compound has a rupture energy expressed in joules per square centimeter or almost twice as reasonably good Butyl tread compound. By this criterion, then, Butyl should rupture or abrade to a greater extent than GR-S. Our experience does not confirm this supposition. To resolve this anomaly, the property of dynamic softness must be introduced into the Schallamach concept, which has been extended to a rough surface in Figure 17.

The rough surface can be likened to an area filled with needle points. In part A of Figure 17 a dynamically hard rubber is pictured. This material will tend to ride on the points of roughness so that load per unit contact area is high. Gouging then would be facilitated.

In part B a dynamically softer rubber is depicted conforming more to the surface roughness. Load per unit contact area is decreased. The more pliable

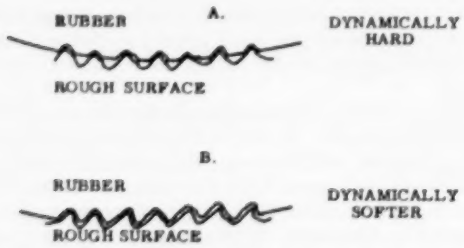

FIG. 17.—Extension of Schallamach concept to rough surface.

rubber would have less tendency to be gouged, provided rupture resistance is not impaired.

The abrasion of rubber then will be related to function of surface friction, strength of the material, and degree of dynamic hardness. These variables have been set up in the following empirical equation:

$$\text{Abrasion loss} = \frac{\text{Dynamic modulus}}{\text{strength}} \times \text{friction}$$

Strength = Area under stress-strain curve which is the rupture energy, R, in joules.

Dynamic Modulus = K, dynes/cm.^{2}—determined under forced vibration—10% extension and 16 cycles per second.

Friction = is related to electrical energy to the magnetic brake of the abrader. This is given in amperes since a constant d.c. voltage is used.

The equation then becomes:

$$\text{Abrasion loss/amp.} = \phi\, K/R$$
$$\text{Cc/km/amp.} = \phi\, K/R$$

Where ϕ is a proportionality constant.

In simple terms, then, this concept states that what is needed for best abrasion resistance is a soft yet tough material.

COMPOUND PROPERTIES AND ABRASION

The above concept is the route by which improvements in abrasion of Butyl compounds have been sought. As will be pointed out in the following section, mixing procedure, compounding ingredients, and state of vulcanization

TABLE 3

Compound	Dyn. mod. (dynes/cm.^{2})	Rupture energy (joules)	$K/R^{+1/2}$	Abrasion loss (cc./km./amp. 18% slip)
Control Mix GR-I-17,* MPC Channel Black	6.0×10^7	131	4.6	.39
Heat Treat Mix GR-I-17* MPC Channel Black	5.1×10^7	130	4.0	.27
GR-S, Tread	7.7×10^7	180	4.2	.28

* Enjay Butyl 217.

affect the ratio of K/R, and thus the resistance to abrasion. It must be admitted at this point that the physical properties of the compounds were determined at rates of deformation different from those encountered in the high-speed operation of a tire tread. The rupture was determined at extension rates of 20 inches per minute and dynamic modulus at 16 cycles per second. These conditions were dictated by the equipment available. However, as the data in the remaining sections indicate, the correlations between the ratios of K/R, so determined, and abrasion losses do show definite trends.

Heat treatment.—This relation explains why the heat treatment[8] of Butyl carbon black mixtures is beneficial to tread wear. Its sole function is to reduce the dynamic hardness of the vulcanized compound. The ratio of K/R is thus reduced, which predicts a lower abrasion loss. Repeated experiments have confirmed this prediction. An example of this change of properties is shown in Table 3.

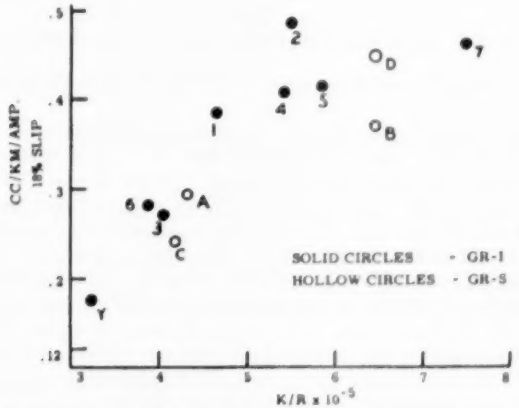

FIG. 18.—Relation between abrasion loss in cc./km./amp. and K/R for seven Butyl tire tread compounds and four LTP GR-S type of tread compounds. Y represents special Butyl tread with optimum properties.

Heat treatment reduces dynamic modulus, with no change in rupture energy. The ratio of K/R is reduced to the same degree as the reduction in abrasion loss. The GR-S tread compound fits into the relation. Its very high rupture energy is balanced by a relatively high dynamic modulus. The resulting ratio of K/R, as well as the abrasion loss, is similar to a good-grade Butyl tread.

Random tire tread compounds.—The mixing, compounding, and curing changes that can be made with Butyl can markedly affect the abrasion resistance. This condition can be shown graphically with a group of seven compounds mixed for tire tread purposes. They contain 50 parts of MPC channel black from two different sources and embrace a wide variation of mixing techniques. Their respective ratios of K/R and abrasion losses are spotted graphically in Figure 18 as solid circles, numbers 1 through 7. Although somewhat scattered, the pattern of points extends from low loss and low K/R to high loss and high K/R values. Points 6 and 3 represent heat-treated mixes, wherein care was taken to maintain the extensibility or elongation of the subsequent vulcanized compound. Points 1 and 2 are control mixes. Points 4, 5, and 7 represent mixes that result in low dynamic moduli, but the extreme mixing

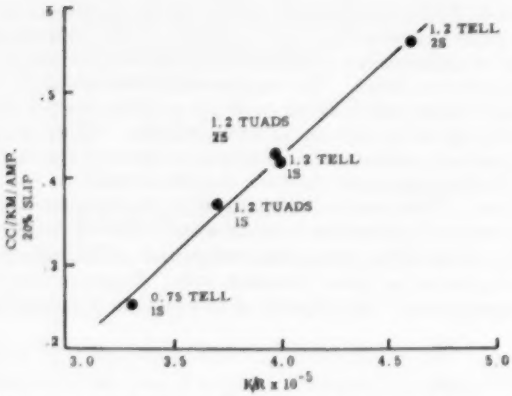

FIG. 19.—Effect of state of cure of Butyl tread compounds on abrasion.

conditions have dangerously lowered extensibility, which in turn reduces rupture energy.

The hollow circles A, B, C, and D are representative cold rubber GR-S treads. Points A and C are GR-S treads with MPC and SAF carbon black, respectively, with very high rupture energy. Point B is a GR-S compound purposely vulcanized to a low extensibility by adding three parts of sulfur, which is an excessive amount. The lowered rupture energy increases the ratio of K/R and increases the abrasion loss. The same is true for point D, where the GR-S tread is cured with only one part of sulfur. Unlike Butyl, reduction of sulfur to one part in GR-S treads results in lowered rupture energies.

Solid circle Y, in the extreme lower left of Figure 18, represents an attempt to cure a heat-treated Butyl so that optimum extensibility and rupture energy are insured. This vulcanizate from one part of sulfur and 0.75 parts of Tellurac[9] represents an improvement over the better Butyl vulcanizates as well as the GR-S reference compounds. It is possible that Butyl tires produced so far may have been overcured from the standpoint of abrasion resistance.

State of vulcanization.—Figure 19 shows just how sensitive a Butyl tread compound is to changes of state of cure. This figure represents a series of

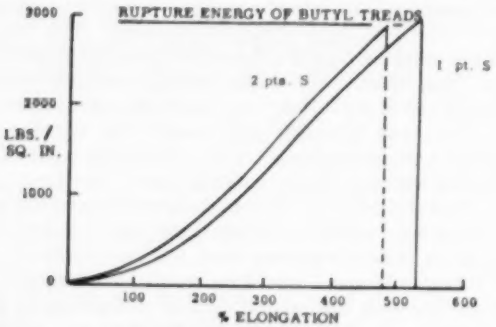

FIG. 20.—Rupture energy of Butyl tread compounds vulcanized with one part and two parts of sulfur.

compounds prepared from the same masterbatch of Butyl and channel carbon black. Extent of cross-linking was controlled by the amount of curatives (sulfur and accelerator) added to the compound after heat treatment. Reducing the sulfur content limits the extent of cross-linking that can be obtained, and extensibility is therefore maintained even at long cure times.

Figure 20 displays two stress-strain curves of the same Butyl-carbon black mixture. The one showing the greater rupture energy (greater area under curve) is vulcanized with only one part of sulfur. This feature is imporant in the vulcanization of large articles, wherein the surfaces are subjected to high

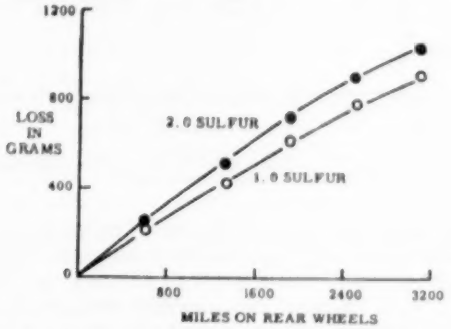

FIG. 21.—Weight loss of Butyl tire treads during road wear tests.

vulcanization temperatures for longer periods of time than the centers. Since Tellurac is such an efficient catalyst for the addition of sulfur to polymer, reduced concentrations of this compound are recommended for optimum abrasion resistance.

Road tests on Butyl tire treads have confirmed the superiority of Butyl compounds whose degree of cross-linking has been minimized by reduced sulfur contents. Figure 21 shows the results of a tread wear test conducted on just the rear wheels of a car. Tires were alternated left to right and weighed every 600 miles. The compound with only one part of sulfur consistently showed about 15 per cent lower abrasion loss. Laboratory abrasion may show as

TABLE 4

SULFUR CONTENT AND ROAD WEAR—50-PART MPC

2 Parts S	—	1221 cc. loss
1 Part S	—	1044 cc. loss

much as a 30 per cent advantage for a compound with reduced sulfur. Another road wear test wherein tires were rotated to all four wheel positions again showed the advantage of reduced sulfur dosages. After 4000 miles, abrasion loss values are shown in Table 4.

These tests were made under severe conditions of braking and cornering.

EFFECT OF PLASTICIZERS AND CARBON BLACK

The tensile properties and dynamic behavior of Butyl can be markedly changed by additions of plasticizer oils and variations of carbon black type. These wide changes in strength and dynamic softness produce the wide vari-

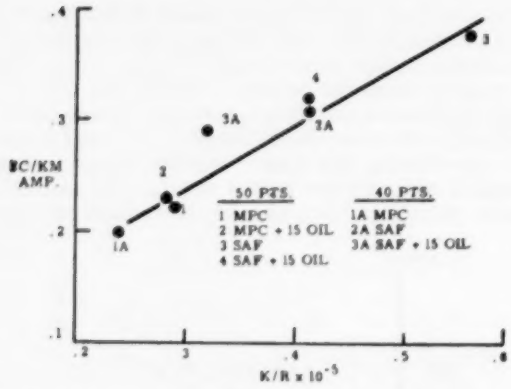

FIG. 22.—Effect of compound changes, carbon black type and plasticizer, on abrasion losses of Butyl rubber treads.

ation in abrasion losses observed in Figure 22. This series of seven compounds, with the compounding changes listed in the small table that accompanies the figure, follows rather closely the relation of abrasion loss and ratio of K/R. Since SAF carbon black (50 parts) produces such dynamically hard compounds, the presence of oil plasticizer makes a great change in the abrasion losses observed. This is observed when points 3 with 4 are compared. With MPC channel carbon black the presence of oil has little effect on abrasion loss, because the ratio of K/R, as shown by points 1 and 2, has not been changed.

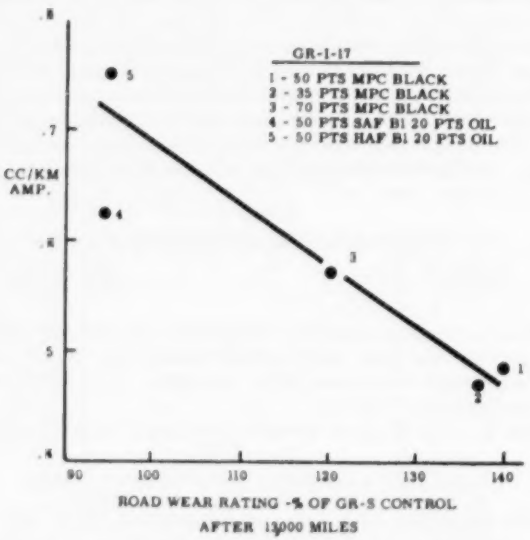

FIG. 23.—Correlation between laboratory abrasion losses and road wear ratings for various Butyl rubber treads.

TABLE 5

PROPERTIES OF BUTYL POLYMERS OF INCREASING MOLECULAR WEIGHT

Polymer Mol. wt. (mv)	GR-I-15* 390,000	GR-I-18† 450,000	B439‡ 750,000	A605‡ 900,000
Rupture energy	127	151	176	186
Dyn. Mod. (dynes) $\times 10^{-7}$	4.3	4.0	4.0	3.6
$K/R \times 10^{-5}$	3.4	2.6	2.3	2.0
Abrasion loss 20% slip cc./km./amp.	0.32	0.30	0.28	0.21

* Enjay Butyl-215.
† Enjay Butyl-218.
‡ Enjay Butyl Experimental Polymers.

Point 1A, with 40 parts of MPC carbon black represents a good balance between rupture energy and dynamic softness.

Although the main purpose of the laboratory work is to evolve some general principles of abrasion to guide our experimental work, some correlation with actual road wear is of interest. Laboratory abrasion values obtained with compounds actually placed on road tests in Texas have given a confident degree of correlation. In Figure 23, for example, the laboratory abrasion loss of five compounds incorporating changes in carbon black and oil content is related to road life ratings expressed as a percentage of a GR-S commercial control. With these road rating values, a high number is superior; while our laboratory tests were expressed in actual volume losses. Here a low number is desirable. The values plotted appear to be good correlations in this inverse fashion.

POLYMER VARIABLES AND ABRASION

Since abrasion is a rupture process, the more perfectly vulcanized network should result in lower abrasion losses. Even micro-flaws can be points of rupture initiation. A reduction of network flaws would result in higher rupture energies, with no increase in hardness.

MOLECULAR WEIGHT

One way to achieve higher rupture energies without an increase in dynamic hardness is to raise the molecular weight of the polymer. In fact, the more perfect vulcanized network obtained with a high molecular-weight polymer would

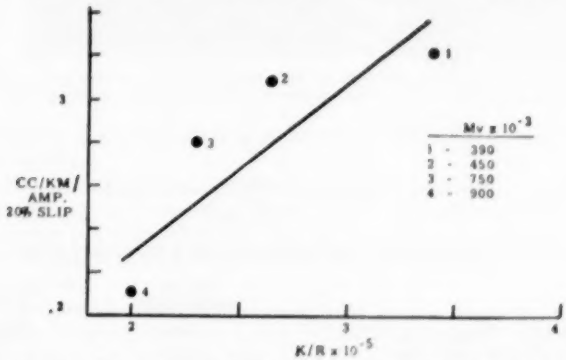

FIG. 24.—Relation between Butyl rubber molecular weight and abrasion loss of tread compounds.

tend toward improved hysteresis properties. A series of increasing molecular weight Butyl polymers confirms the advantages of higher molecular weight. Four polymers were compounded with 50 parts of MPC channel black and three parts of a hydrocarbon oil. Only one part of sulfur was used to minimize differences in unsaturation with the conventional 1.2 parts of Tuads as an accelerator. The polymers used and their compounded properties are given in Table 5.

A plot of abrasion loss and K/R, in Figure 24, predicts that an improved wear-resistant tread could be produced from high molecular weight Butyl.

POLYMER UNSATURATION

Unsaturation in a Butyl polymer limits the maximum extent of cross-linking, just like a reduction in the amount of sulfur in the compound. In fact, a polymer of lower unsaturation will duplicate the abrasion resistance of more of the unsaturated varieties wherein the sulfur content has been reduced. To show this effect, abrasion results with a series of four Butyl rubbers with the following molecular characteristics have been plotted in Figure 25.

These polymers were compounded in a tread compound using 50 parts of MPC channel black per 100 of Butyl. Each type of tread was then vulcanized with two parts and with one part of sulfur, to make eight vulcanizates in all. Their abrasion loss and respective values of K/R follow the established relation fairly well. Abrasion losses increased with increased unsaturation at any given sulfur dosage. The first number adjacent to the various points is the unsaturation expressed in mol-per cent. The number and letter in parentheses in Figure 25 refers to the amount of sulfur. Thus the worst compound from the standpoint of abrasion loss is the one made from GR-I-25 (1.9 unsaturation),

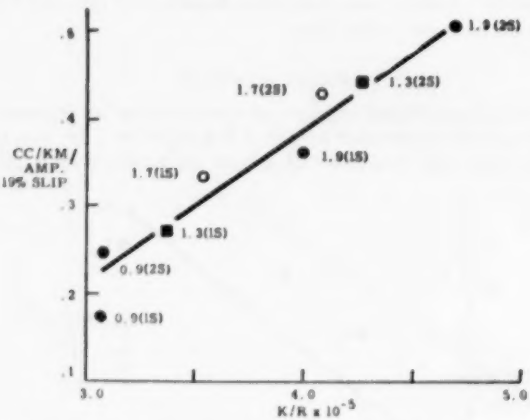

FIG. 25.—Polymer unsaturation and abrasion loss of Butyl rubber treads.

	Mol.-% unsaturation[19]	Viscosity ave. mol. wt.
GR-I (R2) (Enjay Butyl 035)	0.9	325,000
GR-I (Enjay Butyl 150)	1.3	310,000
GR-I-15 (Enjay Butyl 215)	1.7	350,000
GR-I-25 (Enjay Butyl 325)	1.9	325,000

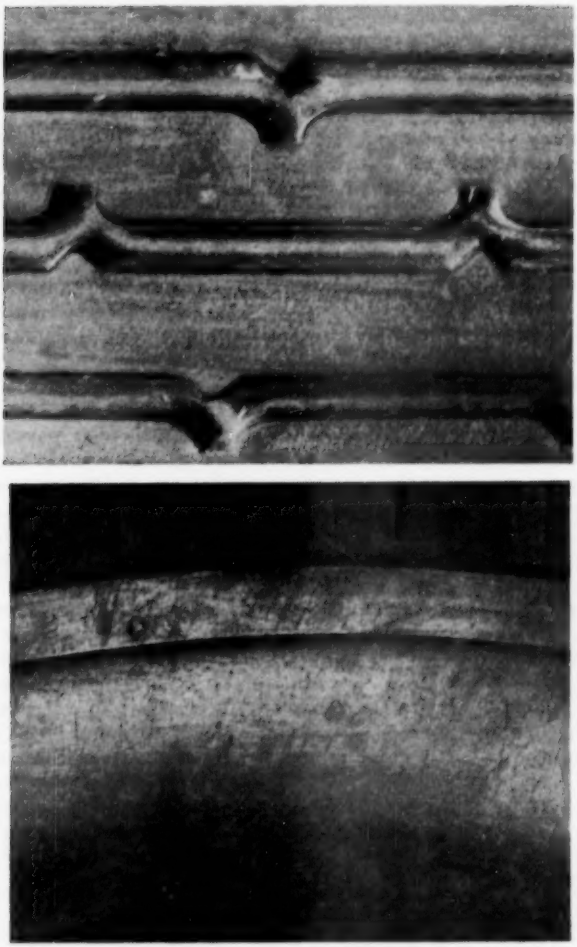

FIG. 26.—Close-up of tread and sidewall of experimental Butyl tire showing, at top, freedom from tread cracking, and, below, absence of weather cracking of sidewall after 25,000 miles of road wear.

using two parts of sulfur. Reduction of sulfur to one part, as shown, results in an improvement.

With the other Butyls, a step-down in unsaturation reduces abrasion losses, and each polymer is further improved by the reduction of sulfur. The very lowest unsaturated Butyl, 0.9 per cent unsaturation, is superior to all others, even with two parts of sulfur, since the extent of vulcanization is limited by the molecular nature.

The questionable value of too low a state of cure is shown in the very last point with one part of sulfur in GR-I (R2). Here a sticky vulcanizate results in an abnormally low abrasion loss. Reduction of unsaturation has, of course, one serious drawback. Rate of cure would be seriously impaired. From an

economic standpoint, then, it would be more practical to obtain low abrasion loss with a higher unsaturated polymer vulcanized in the presence of reduced quantities of sulfur.

SUMMARY

By using the Lambourn abrader, a concept of abrasion has been proposed that fits the performance of a wide variety of compounds. The ability of this type of machine to give varying degrees of slip and braking forces has aided in the selection of the proper conditions for abrasion studies. By using a small tread pattern on the sample wheel, laboratory results are brought into closer agreement with actual road wear tests.

The work of Schallamach and the analysis of abrasion by a needle abrader have been extended to an abrasive surface. To the considerations of compound strength and surface friction or traction has been added the consideration of dynamic hardness. The abrasion of rubber has then been related to a ratio of dynamic modulus over rupture energy. Thus if a compound is made dynamically softer or more conformable without a sacrifice of its resistance to rupture, a superior abrading tread will result. In simple terms, what is needed for best abrasion resistance is the softest toughest material.

Butyl owes its comparable or superior abrasion resistance (compared to other rubbers) to the fact that its vulcanizates are dynamically softer. The heat treatment of Butyl carbon black mixtures produces vulcanizates that are still softer in relation to their rupture energy. This is the sole advantage of such a mixing procedure.

Other polymer and compounding variables that tend to decrease the ratio of dynamic hardness to rupture energy improve abrasion resistance. These changes include increasing the molecular weight of the polymer and reducing somewhat the unsaturation. A certain quantity of plasticizer to increase softness and a reduction of the state of cure have been shown to be beneficial. The latter change produced by a reduction of the amount of sulfur in the compound, which limits the extent of cross-linking, has resulted in distinctly superior tire treads.

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POWER TRANSMISSION—SLIPPAGE-ABRASION. AN INVESTIGATION OF THE ABRASION OF TREAD COMPOUNDS *

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INTRODUCTION

While the investigation described in this paper was underway, Kainradl published a review of the literature on the abrasion testing of vulcanized rubber[1], in which various German and foreign methods were discussed critically. Based on his review, Kainradl came to the conclusion that there is at the present time no generally accepted and useful method for measuring the abrasion of vulcanized rubber compounds which gives results corresponding to road tests of tires, and he put the question whether, even in principle, any laboratory test can be expected to reproduce the general behavior of rubber in road tests.

Based on these considerations, it is recommended that no new type of testing methods be developed at this time, but that the more important methods already available be studied more closely, in particular the methods of constant energy. Meantime Powell and Gough[2] have reported some results which they obtained by this method.

* * * *

It was the purpose of the present work to study the abrasion characteristics of vulcanizates of the tire-tread type under conditions which would reproduce, as closely as practicable, conditions actually prevailing in service. It is on this basis that the following requirements for the test were formulated.

(1) Discontinuous impulse-type of abrasion, such as exists in the rotation of a tire.

(2) Range of slippage corresponding to that existing in service performance, i.e., from 0 to a maximum of 10 per cent.

(3) Operation of the laboratory test with a rotating test-specimen.

Slippage takes place whenever power is transmitted to two mutually rotating surfaces, and, based on the abrasion forces appearing at the contact zone, this power exceeds a critical value which depends on the coefficient of friction, the surface of contact, and the pressure.

For a driven tire, which is the only case which will be considered here, the power transmitted depends on the speed, load, and grade of the road.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk und Gummi*, Vol. 8, No. 9, pages WT227-233, September 1955.

TABULATION AND DEFNITIONS OF THE FACTORS USED IN THE EXPERIMENTS

A	Abrasion $= \frac{\text{Amount of rubber abraded}}{\text{Time of running}}$	mg. per min.
a	Specific abrasion $= \frac{\text{Abrasive wear}}{\text{Abrasion power}} = \frac{\text{Amount of rubber abraded}}{\text{Energy of abrasion}}$	mg./watt-min.
W	Power (total)	watts
W_t	Power transmitted, i.e., the power delivered by the brake generator	watts
S	Slippage	percentage
W_A	$S \cdot W_t$ = abrasion power	watts
T	Temperature	Centigrade
λ	Heat conductivity	kcal./m.-hr.-degree
K	Temperature coefficient of conductivity $= \frac{\lambda}{c \cdot \rho}$	cm.²/sec.
ρ	Density	g./cc.
c	Specific heat	cal./g.-degree
i	Heat convection	watts
j	Heat convection density $= i/F$	watts/cm².
F	Surface area	cm².
τ	Time interval	sec.

Rubber Compounds Studied

A_1	Natural rubber + 45 parts CK-4 carbon black
A_2	Natural rubber + 45 parts HAF black
A_3	Natural rubber + 45 parts ISAF black
A_4	Natural rubber + 20 parts silica
B_1	GR-S (cold rubber) + 45 parts CK-4 carbon black
B_2	GR-S (cold rubber) + 45 parts HAF black
B_3	GR-S (cold rubber) + 45 parts ISAF black
C	Vulkollan (Shore hardness 70).

ABRASION MACHINE AND PRINCIPLE OF MEASUREMENTS

THE MACHINE

The machine operates on the principle of the Dunlop-Lambourn machine. It is shown schematically in Figure 1.

A grinding wheel S, driven by motor M, drives, through the medium of a small rubber wheel R which is the abrasion test-specimen, a direct-current generator G, whose power output is controllable and is measured by a wattmeter W. The slippage between the test-specimen and grinding wheel is measured by a photoelectric count of the number of rotations of the two. The grinding wheel can be made up of various materials. In the abrasion experiments described, a silicon carbide wheel (grain 36, hardness 46) was found to give the best results.

The type of test-specimen is a solid rubber tire of 70 mm. diameter and

bearing surface 10 mm. wide, which was mounted on a shaft of 35 mm. diameter. The grinding wheel is provided with a heating coil so that the surface temperature of the wheel can be regulated at any temperature from 20° to 100° C. The measurements were actually made only in the range of 20°–70° C, since above 70° C, the well known smearing effect appears and disturbs the process of abrasion.

PRINCIPLE OF THE MEASUREMENTS

Power distribution in the abrasion machine.—The power required to drive the machine consists of the abrasion power, the power transmitted, and the frictional losses in the bearings:

$$W_0 = W_A + W_t + W_v \tag{1}$$

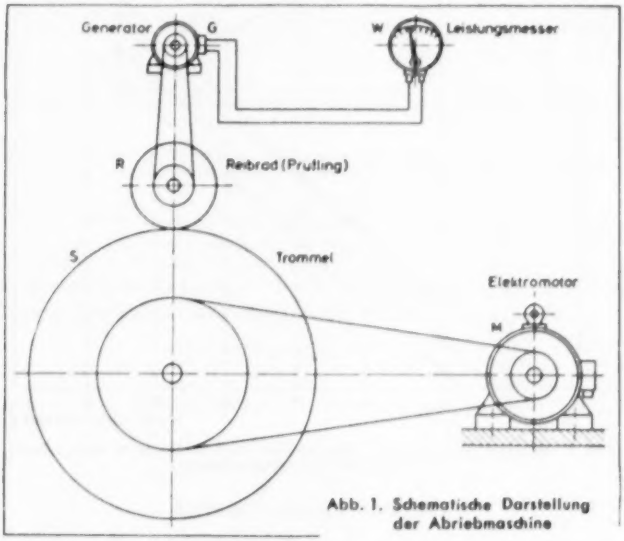

FIG. 1.—Schematic representation of the abrasion machine. On the diagram, Leistungsmesser wattmeter; Reibrad grinding wheel (test-specimen); Trommel drum.

where W_t is the power measured at the generator, and W_v is small enough to be disregarded. If S is the slippage, then the power of abrasion W_A is:

$$W_A = S \cdot W_t \tag{2}$$

The abrasion power is, in turn, partly consumed in the actual abrasion process, W_W, and is partly transformed into heat, W_H.

$$W_A = W_W + W_H \tag{3}$$

Method of measurement.—The test-specimen is run for 5 minutes under a constant transmitted power W_t, during which period the slippage S is measured. The applied pressure is always kept at 3.5 kg. per sq. cm. The abrasion loss is determined by weighing. Every measurement recorded is the mean value of at least five individual measurements.

EXPERIMENTAL RESULTS

SLIPPAGE CHARACTERISTICS

Figure 2 shows the slippage as a function of the power transmitted. Up to a load W_c, the value of which is characteristic of each individual vulcanizate, power is transmitted without any slippage. As soon as W_t exceeds W_c, slipping begins, and this increases as a linear function of W_t. The slope of a slippage line on the graph has a value which is characteristic of each vulcanizate, and this slippage can be expressed in the form of Equation (4):

$$S = S_0 \cdot (W_t - W_c) \tag{4}$$

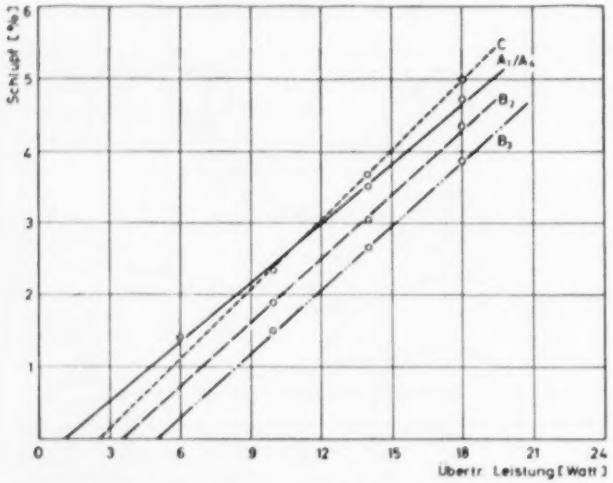

FIG. 2.—Slippage characteristics. The abscissa indicates the power transmitted; the ordinate the percentage slippage.

ABRASION CHARACTERISTICS

Abrasion takes place as soon as slipping begins, i.e., when $W_t > W_c$. Up to a specific critical slippage $S_{crit.}$, which is characteristic of each individual vulcanizate, the abrasion increases as the square of the power transmitted, as expressed by Equation (5) and Figure 3:

$$A = A_0(W_t - W_c)^2 \tag{5}$$

If the abrasion is plotted against the abrasion power: $W_A = S \cdot W_t$ (see Figure 4), straight lines passing through the axis are obtained, i.e., a linear relation, as represented by Equation (6):

$$A = a \cdot W_A = \frac{1}{W_W} \cdot W_A \tag{6}$$

It is possible, therefore, to define, for every vulcanizate, a specific abrasion value a (e.g., expressed in mg./watt × min.) and a specific abrasion energy $W_W = \frac{1}{a}$ (e.g., in watt^{-1} × min./mg.).

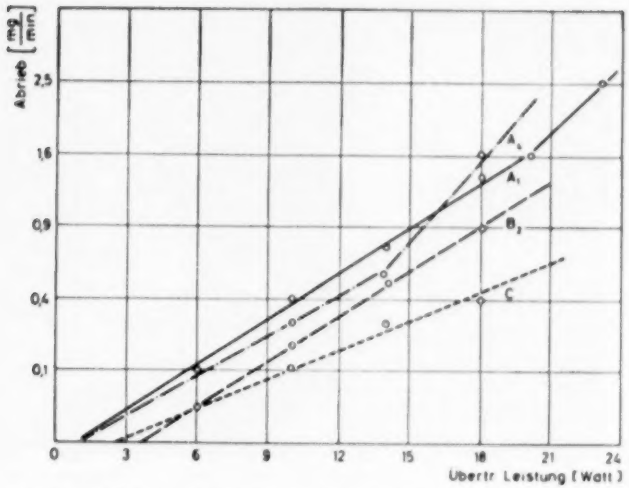

FIG. 3.—Abrasion characteristics. The abscissa indicates the power transmitted; the ordinate the abrasive wear in mg. per mm.

DEPENDENCE OF THE SPECIFIC ABRASION ON TEMPERATURE

The abrasion of a vulcanizate with constant abrasion power increases linearly with rise of temperature. In the temperature range of 20° to 70° C, the relation is expressed by Equation (7) (see Figure 5):

$$(a_T - a_0) = \alpha_0(T - T_0) \tag{7}$$

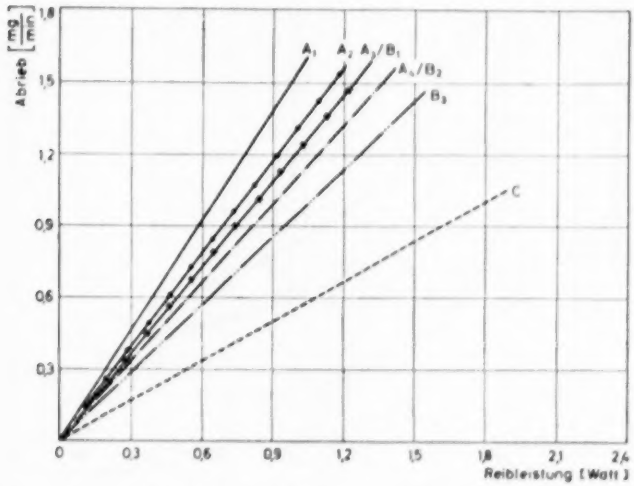

FIG. 4.—Abrasion as a function of the abrasion power. The abscissa indicates the abrasion power; the ordinate the abrasive wear.

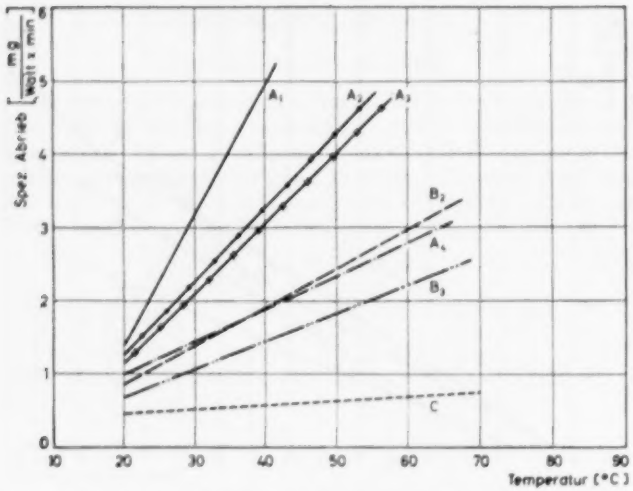

FIG. 5.—Specific abrasion as a function of the temperature. The ordinate indicates the specific abrasion in mg./watts × min.

where a_T is the specific abrasion at temperature T and a_0 is the specific abrasion at temperature T_0.

Analogous to the relation shown in Figure 5, Figure 6 shows the dependence of the specific abrasion energy on the temperature. The course of the curves in Figure 6 indicates, in the opinion of the author, that, for a better understanding of the abrasion process, the specific abrasion energy must be measured at low temperatures as well, a problem which at the present time is being attacked,

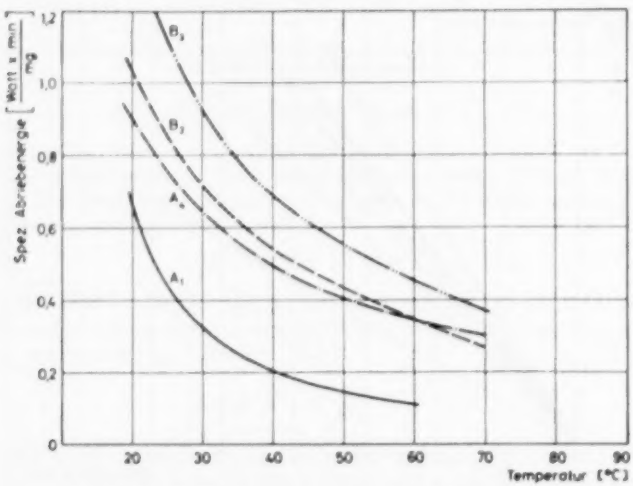

FIG. 6.—Specific abrasion energy as a function of the temperature. The ordinate indicates the specific abrasion energy.

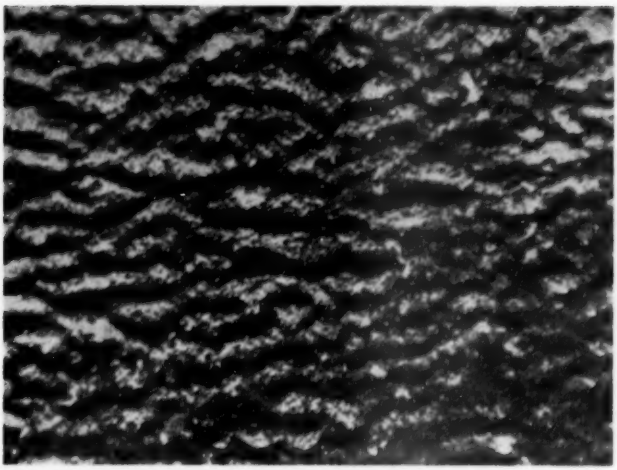

FIG. 7.—An abrasion pattern (magnification 175).

but which has not yet led to any definite conclusions. Preliminary measurements indicate that the specific abrasion energy passes through a maximum value at a temperature lying between 10° and 20° C which is characteristic of each vulcanizate, and then decreases again at lower temperatures.

THE CRITICAL SLIPPAGE VALUE

Above a critical slippage, S_{crit}, the value of which is characteristic of every vulcanizate, the quadratic dependence of the abrasion on the power transmitted, as expressed by Equation (5), no longer holds true, and the abrasion

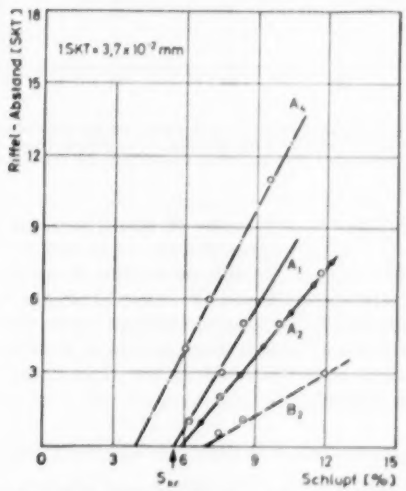

FIG. 8.—Space between ridges as a function of the slippage. The abscissa indicates the percentage slippage; the ordinate the space between ridges. The arrow on the abscissa points to the critical slippage.

increases rapidly. This phenomenon was studied in detail by Ebert and Weidner[3]. In the present work, the author was able to confirm the general course of the abrasion-slippage curves of these investigators.

For slippage values where $S > S_{crit}$, the socalled abrasion patterns described by Schallamach[4] appear. These abrasion patterns take the form of parallel ridges, which lie perpendicular to the direction of abrasion (see Figure 7). The distance apart of these ridges increases linearly with the slippage (see Figure 8). By extrapolation of the straight lines in Figure 8, a slippage value S_{crit} characteristic of every vulcanizate is obtained, and this value is identical with the value defining the characteristic abrasion.

Schallamach has pointed out in this connection that the appearance of these abrasion patterns is associated with a considerable increase of the abrasion. He subjected a test-specimen to abrasion in a fixed direction, as a result of

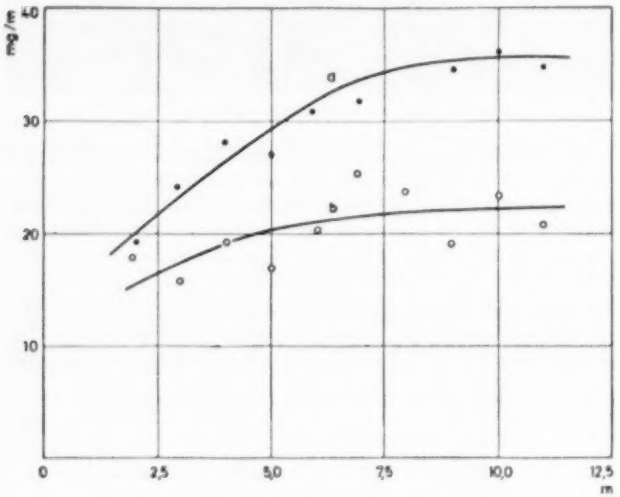

FIG. 9.—Dependence of the amount of abraded rubber on the time of running[4] (in mg. per 50 cm. travel). (a) Test-specimen abraded in a fixed direction. (b) Test-specimen turned 90° after each 50 cm. travel. The abscissa indicates the travel in meters; the ordinate the amount of rubber abraded in mg. per m.

which the loss by abrasion per meter of travel increased in accordance with curve *a* in Figure 9. After approximately 10 meters travel, this loss reached a constant value per meter. At this point, the abrasion pattern also had become completely developed. If, on the other hand, the formation of an abrasion pattern is prevented by turning the test-specimen 90° from the direction of abrasion each half meter of travel, then the rate of wear is represented by curve *b* in Figure 9. The rate is obviously slower than under conditions where an abrasion pattern is formed.

COMPARISON OF DIFFERENT ABRASIVE SURFACES

The specific abrasion energy, i.e., the energy which is required to wear away a definite amount of rubber, depends on the grinding surface. Figure 10 shows

a comparison of a rough iron surface, a silicon carbide wheel, and a polished iron surface, tested comparatively with vulcanizate A_1 at 20° C.

TEMPERATURE OF ABRASION

The abrasion power converted into heat is manifest in the temperature of abrasion. Figure 11 shows the temperature as a function of the abrasion power, measured by a thermoelement inserted in the surface layer about 0.3 mm. deep, of a test-specimen of vulcanizate B_1. The temperature rises linearly with the work of abrasion in accordance with Equation (8).

$$T_A - T_0 = \theta \cdot W_A \tag{8}$$

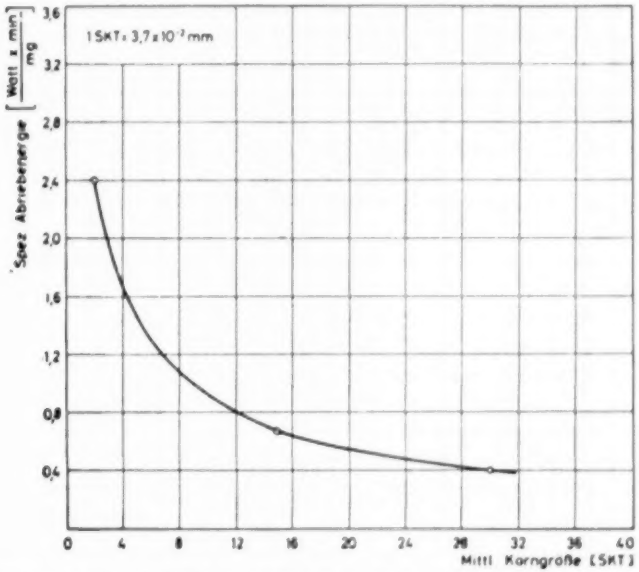

FIG. 10.—Specific abrasion energy as a function of the grain size (roughness) of the grinding surface. The abscissa indicates the mean grain size in SKT units (1 SKT = 3.7×10^{-2} mm.); the ordinate the specific abrasion energy.

For the silicon carbide wheel, the measured value of θ was 4° C/watt. When an iron wheel was used, no measurable rise of temperature during abrasion was manifest.

Because of the character of the testing method, no brief localized high flash temperature can be detected in the measurements, such as is found in the abrasion of metals and certain nonmetallic solid materials[5] and also has been suspected at times in the case of rubber; instead, a mean value for the time of test is measured. These temperature relations will be discussed in more detail later (see the Discussion of the Experimental Results).

CORRELATION BETWEEN ROAD WEAR AND LABORATORY ABRASION

An essential prerequisite for a satisfactory correlation[6] between road tests and laboratory tests is, as has always been, that the test conditions simulate the

service conditions. With respect to the use of the vulcanizates already tested for tire treads, the following conditions had, therefore, to be fulfilled.

First was the use of a rotating abrasion test-specimen, with slippage values and loads corresponding to those of tires in actual service. These requirements mean, in the final analysis, that the severity of the abrasion in the laboratory test must conform to that prevailing in service. By severity of abrasion is meant:

$$\text{Severity} = \frac{\text{Wear of tire tread in mm.}}{\text{No. of turns of tire}}$$

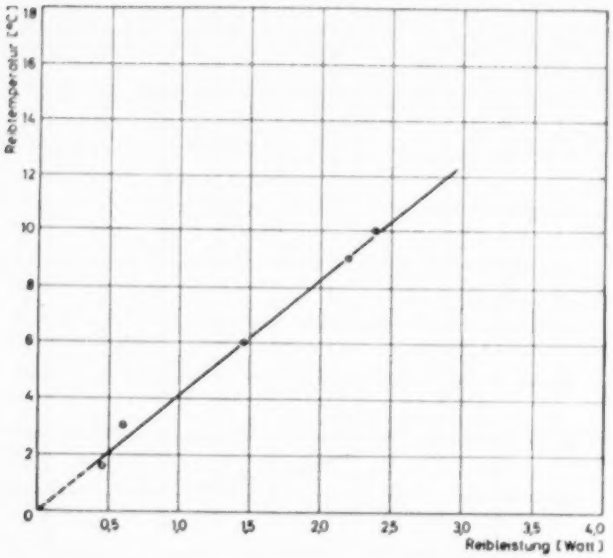

FIG. 11.—Temperature of abrasion as a function of the abrasion power. The abscissa indicates the abrasion power; the ordinate the temperature of abrasion.

A simple estimation shows that this condition is fulfilled in the present case when, for a tire with a 10-mm. tread and 40,000 km. road performance, the severity of abrasion is:

$$\frac{10 \text{ mm.}}{4 \times 10^7 \text{ m.}} = 2.5 \times 10^{-7} \frac{\text{mm.}}{\text{m.}} \approx 5 \times 10^{-7} \frac{\text{mm.}}{\text{turns}}$$

For the abrasion test-specimen in the present work with contact surface width of 10 mm. and circumference of 20 cm., the severity of abrasion was, at a mean specific abrasion of 1.2 mg. per min. and r.p.m. of 1200, which corresponded to a rotation frequency of 20 cycles per sec., as follows:

$$1.2 \frac{\text{mg.}}{\text{min.}} = \frac{1.2 \text{ mg.}}{1.2\ 10^3 U} = 10^{-3} \text{ mg./}U \approx 10^{-6} \frac{\text{cc.}}{\text{turn}}$$

This corresponds, with a surface of 20 sq. cm. of abraded layer, to:

$$\frac{10^{-6} \text{ cc.}}{20 \text{ sq. cm.}} = 5 \times 10^{-8} \text{ cm.}/U = 5 \times 10^{-7} \text{ mm./turn}$$

When these figures are examined, it becomes evident how much more severe the test conditions of many laboratory abrasion tests are, particularly the test method carried out in accordance with DIN-53-516, in which a layer several mm. thick is abraded away in only 2.5 minutes and a travel of 40 meters, with 100 per cent slippage. Under these conditions, any satisfactory correlation between road wear and laboratory abrasion data cannot even be expected.

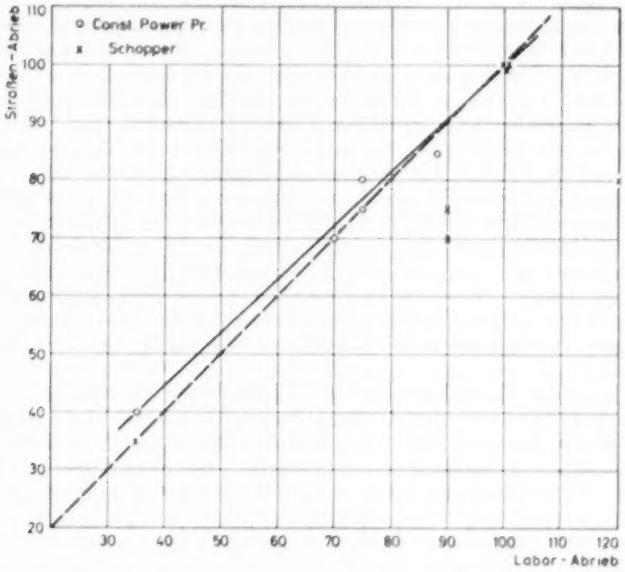

FIG. 12.—Correlation between road tests and laboratory tests. The abscissa indicates the laboratory abrasion; the ordinate the road wear.

Figure 12 shows the correlation between road wear and laboratory measurements for the method of DIN-53-516 and with the principle of constant energy. Under these conditions, when the abrasion test-specimens undergo slippage which exceeds the critical slippage value, the abrasion patterns of Schallamach naturally appear, and there can be no strict correlation with road tests where conditions are not severe enough for abrasion patterns to appear. Furthermore we have been able to prove that, in road tests, the abrasion patterns, which depend on a considerable increase of abrasion, appear only at high slippage values.

DISCUSSION OF THE EXPERIMENTAL RESULTS

WEAR OF METALS

Shaw[7] and others have demonstrated that the specific abrasion energy of a crystalline substance, e.g., a metal, increases with decrease of the size of the

particles abraded away and finally reaches a limiting value for a particle size of approximately 5×10^{-5} cm. This critical size of particle is related directly to local disturbances of the crystal structure.

THE ABRASION BEHAVIOR OF VULCANIZED RUBBER

If these facts are applied to rubber, it is, of course, impossible to specify a critical particle size based on crystal structure or any corresponding critical specific abrasion energy. However, it can be assumed that the maximum energy in the extreme case tends towards the energy of chemical combination of rubber and filler.

Assuming an energy of combination of 80 kcal. per mole and a mean particle size of 38μ in a natural rubber *C* black system, Powell and Gough[2] calculated a specific abrasion energy of 0.5×10^{-4} kcal. per g. $= 3.3 \times 10^{-6}$ watt-min./mg. The values measured by the present author are, for a rough iron surface, 0.4 watt-min./mg. = 6 kcal./g. for the silicon-carbide wheel, 0.7 watt-min./mg. = 10 kcal./g., and for the polished iron wheel, 1.8 watts-min./mg. = 25 kcal./g.

For three different abrasion machines, the du Pont machine, the Lambourn machine, and the B.S.A.T.R.A. machine, all of which operate on the principle of constant energy, Powell and Gough found values of 5.4, 4.1, and 0.25 kcal./g. With decreasing degree of roughness of the abrasive surface, and corresponding decrease of particle size of the abraded rubber particles, the specific abrasion energy increases here too, just as is to be expected from the example of the behavior of metals. However, its absolute values are too high by a factor of 10^5. In this way rubber can be contrasted with metals, for which the measured values agree satisfactorily in their order of magnitude with the theoretical values.

As has already been expressed in Equation (3), the measured abrasion energy is made up of two components, the energy consumed in the actual process of abrasion, and a second component, energy which is absorbed in the boundary surface and is transformed into heat, without any breakdown of the structure. This energy appears as heat of friction and thereby causes wear as soon as the temperature of decomposition of the rubber is exceeded.

The capacity of the rubber to absorb relatively great amounts of mechanical energy as heat in the contact layer during abrasion accordingly governs the abrasion characteristics of a vulcanizate to an extent which is the greater, the smoother is the abrasive surface. The degree of roughness of this surface is a decisive factor in the energy consumed in any definite breakdown of structure.

ESTIMATION OF THE TEMPERATURE OF ABRASION ON THE ASSUMPTION THAT THE TOTAL POWER IS TRANSFORMED INTO HEAT

In addition, a relation may be given to show the rise of temperature in the boundary layer of abrasion of two media:

$$T - T_0 = \frac{0.964 \cdot j \cdot l}{\lambda_1 + \lambda_2} = \frac{0.964 \cdot i \cdot l}{4l^2(\lambda_1 + \lambda_2)} \tag{9}$$

where j is the density of the heat convection corresponding to the abrasion energy:

$$W_A = S \cdot W_i: \qquad j = \frac{W_A}{F} = \frac{W_A}{4l^2},$$

$2l$ is the edge length of the zone of contact, and λ_1 and λ_2 are the heat conductivity values of the two media.

Equation (9) was derived with the assumption of constant heat convection, i.e., constant abrasion energy with respect to time. This assumption was, however, not fulfilled under the conditions, because the rotating abrasion test-specimen underwent pulsations during the abrasion. Figure 13 shows the time relation of the abrasion power in a rotating surface zone of the test-specimen.

During the impulse time τ_p, a heat convection current, $i_p = W_A$, flows, whereas in the interval τ_0, $i = 0$. Correspondingly the temperature of the boundary layer also shows a pulsating effect, and the temperature fluctuations, analogous to the socalled skin effect in electrical engineering, enter, exponen-

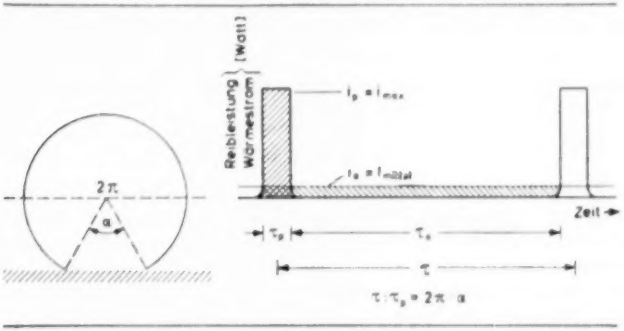

FIG. 13.—Abrasion power during the operating time. On the diagram, *Reibleistung* is the abrasion power; *Wärmestrom* the heat convection, and *Zeit* the time. i_{mittel} is i_{mean}.

tially modified, into the relation[8] in the form of the coefficient of heat conductivity k:

$$(T - T_0)_x = (T - T_0)_0 \cdot \exp\left(-\frac{x}{\sqrt{\frac{k \cdot \tau_0}{\pi}}}\right) \tag{10}$$

After passing through a boundary layer:

$$d_0 = \sqrt{\frac{k \cdot \tau_0}{\pi}} \tag{11}$$

the temperature fluctuations become reduced to $1/e = 35\%$. In our case, with $k = 2 \times 10^{-3}$ cm.²/sec. and $\tau_0 = 5 \times 10^{-2}$ sec., the thickness d_0 of the boundary layer is:

$$d_0 = \sqrt{\frac{2 \times 10^{-3} \times 5 \times 10^{-2}}{3.14}} = 5.5 \times 10^{-3} \text{ cm.} = 0.05 \text{ mm.}$$

The problem can now be treated on the basis of Equation (9) for a point of measurement at distance $x = d$ as stationary, with:

$$i_0 = \frac{\tau_0}{\tau_p} \cdot i_p$$

if $d \gg d_0$, a condition which in the present case is fulfilled for the position of the measuring element with $d = 0.3$ mm. and $d_0 = 0.05$ mm. At a depth of $d = 0.3$ mm. $= 6.d_0$, the temperature fluctuations become only 1/400. The thermoelement is, therefore, no longer influenced by the temperature of the boundary layer.

In the abrasion tests in the present investigation, there is accordingly found on the emery wheel, for an abrasion power of 1 watt, with the values:

$$j = \frac{i_p}{F} = \frac{1 \text{ watt}}{2 \text{ cm.}^2}; \quad 2l = 1.5 \text{ cm.}; \quad \begin{matrix} \lambda_{Gu} = 0.3 \text{ kcal./m.-hr.-g.} \\ \lambda_{sc} = 0.2 \text{ kcal./m.-hr.-g.} \end{matrix}$$

a power value of 1 kcal./hr. = 1.15 watt, a rise of temperature of

$$T - T_0 = \frac{0.964 \times 0.5 \text{ watt/cm.}^2 \times 0.75 \text{ cm.} \times \text{m.} \times \text{hr.} \times \text{g.}}{0.5 \text{ kcal.}} = 65^\circ \text{ C}$$

for the case where the heat convection is maximum. As a time average, however, the heat convection current is only:

$$i_0 = i_p \cdot \tau_0/\tau_p = i_p \cdot (1/13)$$

and accordingly the mean temperature of abrasion is about 5° C per watt of abrasion power. Considering the simplified assumptions in the estimation, this value should be accepted only as an indication of the order of magnitude of the expected temperature of abrasion. However, the relatively good agreement with the measured value might be regarded as a confirmation of the assumption, made on the basis of other considerations, that, from a practical viewpoint, the total abrasion power is consumed in the abrasion boundary layer and is transformed into heat.

CONCLUSIONS

In conclusion, we should like to add that, in spite of some interesting results, the problem of the abrasive wear of rubber can in no way be regarded as solved and that, in our opinion, it is necessary to study further the individual process of abrasion for the purpose of carrying the complex views of the abrasion resistance of vulcanized rubber back to other fundamental properties of rubber.

APPENDIX

CALCULATION OF THE ABRASION ENERGY

Powell and Gough[2] have calculated, on the assumption of a C—C bond energy of 80 kcal./mole $= 5.6 \times 10^{-12}$ erg/molecule and the size of an isoprene elementary cell of 27 Å^3, a surface energy of approximately $\frac{5.6 \times 10^{-12}}{27 \times 10^{-16}} = 2000$ erg/cm^2. Therefore the energy consumed in the formation of a new surface of 1 sq. cm. is 2000 ergs.

In the process of abrasion, new surfaces are being formed continuously. If an abraded particle is assumed to be cubical, with unit dimension x, detachment of the first particle must result in the formation of a new surface of $5\ x^2$, and for all subsequently detached particles a new surface of $4x^2$. Hence for a number $N (N \gg 1)$:

$$F = N \cdot 4\ x^2$$

In the unit volume of 1 cc., $N = 1/x^3$, and consequently $F = 4/x$(cm.²/cc.). For a particle size of 38μ, the authors calculate from this a surface area:

$$F = \frac{4}{38 \times 10^{-4}} = 1050 \text{ (cm.}^2\text{/cc.)}$$

and accordingly an abrasion energy:

$$W_A = 2000 \times 1050 = 2.1 \times 10^6 \text{ (erg/cc.)} = 0.5 \times 10^{-4} \text{ (kcal./cc.)}$$

CALCULATION OF THE TEMPERATURE OF ABRASION

The case considered is one-dimensional. In the abrasion boundary layer between the two materials, with coefficients of heat conductivity λ_1 and λ_2, respectively, the heat convection (see Figure 14) is: $i = S \cdot W_i = W_A$, and

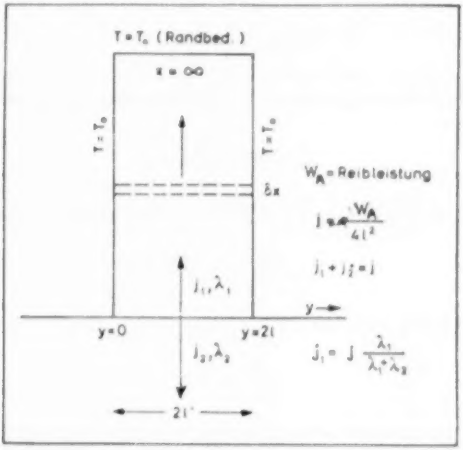

FIG. 14.—Calculation of the temperature of abrasion. From the abrasion test-specimen a rectangle over the contact surface F (marginal length $2l$) with height $x \to \infty$ is cut out. As the marginal condition, $T = T_0$ at the margin of the rectangle is assumed. On the diagram, $T = T_0$ (Randbed.) is $T = T_0$ (marginal condition); W_A = Reibleistung is W_A = abrasion power.

therefore a heat convection density $j = i/(4l^2)$. For an elementary volume, in place of $y = l$:

$$4l^2 \cdot \lambda \frac{d^2T}{dx^2} \delta x - \frac{\lambda}{l} \cdot 8l(T - T_0)\delta x = 0 \qquad (1')$$

as well as the boundary condition:

$$i = 8l \cdot \frac{\lambda}{l} \int_0^\infty (T - T_0)dx \qquad (2')$$

From Equation (1'), a simple differential equation is derived in the form:

$$a \cdot T'' - bT + c = 0 \qquad (3')$$

with the solution:

$$T - T_0 = A \cdot \exp\left(-\sqrt{\frac{b}{a}} \cdot x\right) \qquad (4')$$

With the boundary condition (2′), there is obtained:

$$A = \frac{i\sqrt{2}}{8 \cdot \lambda \cdot l} \tag{5′}$$

The final solution consequently is:

$$T - T_0 = \frac{i\sqrt{2}}{8 \cdot \lambda \cdot l} \cdot \exp\left(-\sqrt{\frac{2}{l}} \cdot x\right) \tag{6′}$$

For the abrasion boundary layer ($x = 0$), the temperature rise is accordingly:

$$(T - T_0)_{x=0} = \frac{i\sqrt{2}}{8 \cdot \lambda \cdot l}$$

Taking into account that, of the heat convection i, the fraction:

$$i_1 = i \cdot \frac{\lambda_1}{\lambda_1 + \lambda_2} \tag{7′}$$

is flowing in the first medium, there is finally obtained, when $j = i/(4l^2)$ the ultimate equation:

$$T - T_0 = \frac{0.7 \cdot j \cdot l}{\lambda_1 + \lambda_2} \tag{8′}$$

Jaeger[9] has derived, by a more precise recalculation of the problem, the equation:

$$T - T_0 = \frac{0.964 \cdot j \cdot l}{\lambda_1 + \lambda_2} \tag{9′}$$

This equation is valid with the limitation:

$$\frac{v \cdot l}{2k_2} < 0.1$$

where v is the rate of abrasive wear, l is the half edge length of the abrasion zone, and k_2 is the coefficient of heat conductivity of the second medium (the grinding base).

For $\frac{v \cdot l}{2k_2} \geqq 0.1$, Equation (9′) becomes:

$$T - T_0 = \frac{0.964 i \cdot l}{4l^2\left[\lambda_1 + 0.88\,\lambda_2\left(\frac{v \cdot l}{k_2}\right)^{0.6}\right]}$$

SUMMARY

The abrasion behavior of vulcanizates of the tire-tread type have been studied by the method of constant energy, with a test apparatus operating on the principle of the Dunlop-Lambourn machine. As a result of this work, the following facts were established.

Up to a critical slippage, the value of which is characteristic of every individual vulcanizate, the abrasion, i.e., the amount of rubber worn off per unit of time, increases with the square of the slippage. The slippage increases linearly with the power transmitted. To this quadratic relation between the power transmitted and the slippage corresponds a linear dependence of the abrasion

power, i.e., it is possible to assign a specific abrasion energy to every individual vulcanizate.

The specific abrasion energy is inversely proportional to the temperature and also inversely proportional to the mean particle size of the abrasive material. A comparison of the measured specific abrasion energy with the corresponding value to be expected by theoretical calculation shows that the experimental value is too high by a factor of 10^4. From this, one is led to the conclusion that the abrasion power is practically completely consumed as heat in the abrasion boundary layer, an idea which is supported by measurements of the temperature of abrasion and a comparison of this with the calculated values.

Above the critical slippage value, the simple linear dependence of the abrasive wear on the abrasion power no longer holds true, and a specific abrasion energy cannot be defined. In addition, the abrasion patterns described by Schallamach then appear, and any correlation between laboratory tests and road wear tests is lost.

ACKNOWLEDGMENT

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RUPTURE OF RUBBER. III. DETERMINATION OF TEAR PROPERTIES *

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INTRODUCTION

A criterion for the onset of tearing, involving a characteristic energy, has been developed and verified by Rivlin and Thomas[1]; the characteristic energy defines a tear property which is independent of the form of the test-piece, unlike the arbitrary tear resistance value obtained by conventional tear tests. It is the purpose of the present paper to apply the energetic considerations embodied in the criterion to the investigation of the tear properties of rubber vulcanizates.

The criterion was developed[1] in the form:

$$-(\partial W/\partial c)_l = T\,h \tag{1}$$

where W is the stored elastic energy of a thin sheet of vulcanizate of thickness h, c is the length of the cut or tear, and T is an energy characteristic of the material. The subscript l denotes differentiation with constant displacement of the boundaries over which forces are applied. A slight change of notation from that of Rivlin and Thomas[1] has been made, in that h has been substituted for t as the thickness of the sheet. As stated by Rivlin and Thomas and elaborated by Thomas[2], T is to be interpreted as the energy expended irreversibly per unit increase of the length of the tear and per unit thickness of the sheet.

It has been shown by Rivlin and Thomas[1] that, by a suitable choice of the shape and dimensions of the test-piece (the test-piece shown here in Figure 1), Equation (1) reduces to a form:

$$T \cdot h \cdot dc = dw \tag{2}$$

which is independent of the elastic properties of the vulcanizate, dw being the work done by the applied forces for an increase dc of the length of the tear. Equation (2) can be applied, not only to the onset of tearing to which the criterion (1) appertains, but also to continuous tearing to which a definite rate of propagation is ascribed; T then denotes the energy, per unit length of tear and per unit thickness, required to propagate the tear at a certain rate, and T will, presumably, be a function of the rate. If this is the case, an adequate description of the tear behavior of a vulcanizate entails the determination of the energy for tearing T as a function of the rate of propagation; a single value for T, defining only the onset of tearing, would be insufficient. That the energy for tearing can, in fact, vary with the rate of propagation may be readily demonstrated, for example, with GR-S vulcanizates by applying various forces to test-pieces of the form shown in Figure 1 and observing the different rates at which the tear propagates.

* Reprinted from the *Journal of Polymer Science*, Vol. 18, pages 189–200 (1955).

In the following sections the measurement of the energy for tearing T as a function of the rate of propagation is described and discussed. Results obtained with natural rubber and GR-S gum vulcanizates are given to illustrate the possibilities of the method for the characterization of tear properties and for the investigation of the nature of the tear process. GR-S and natural rubber have been selected because their vulcanizates differ considerably in rupture properties.

MEASUREMENT OF THE ENERGY AND RATE OF TEAR PROPAGATION

THE TEAR TEST-PIECE

The type of test-piece used in the measurement of the energy and rate of the tear propagation is shown in Figure 1, in both the undeformed and extended states. In the following derivation it is assumed that the thickness h is small so that the couple required to bend the arms is negligible in comparison with the tensile tearing force.

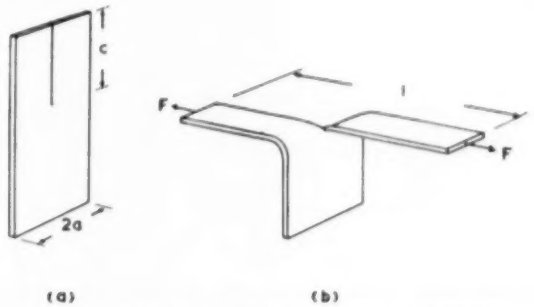


FIG. 1.—The tear test-piece: (a) undeformed; (b) extended.

If a tearing force F is applied to the arms to produce tearing along the central axis and the arms are sufficiently long in comparison with their widths a, there will be a region of each arm which is substantially in simple extension, with an extension ratio λ determined by the force F. For an increase dc of the length of the tear, the region of simple extension in the arms is increased in volume by $2a\,h\,dc$ at the expense of the undeformed region ahead of the tear, a, h, and dc being referred to the undeformed state. The separation l of the grips by which the force is applied is thereby increased an amount dl given by:

$$dl = 2\lambda\,dc \tag{3}$$

From the work of Rivilin and Thomas[1], or as may be seen directly from simple energy considerations, the energy for tearing T is given by:

$$T\,h\,dc = F\,2\lambda\,dc - W_0\,2a\,h\,dc \tag{4}$$

where W_0 is the work done/unit volume in deforming the vulcanizate in simple extension to an extension ratio λ. It has been shown by Rivlin and Thomas, that, if the width $2a$ of the test-piece is sufficiently large, $\lambda \approx 1$ and $F \gg W_0\,ah$. Equation (4) then reduces to:

$$T\,h = 2F \tag{5}$$

If tearing is now considered to be continuous with a rate of propagation dc/dt and $\lambda \approx 1$, the rate of separation of the grips is, from (3):

$$dl/dt = 2dc/dt \tag{6}$$

For test-pieces whose width is sufficiently large, the energy for tearing T may, therefore, be derived from the tearing force F by Equation (5) and the rate of propagation of the tear may be derived from the rate of separation of the grips by Equation (6).

We may note that this test-piece shows the following features:

(1) The relation between F and T is independent of the length c of the tear.

(2) When a is sufficiently large, this relation is substantially independent of a and of the elastic properties of the material.

(3) The rate of propagation of the tear is governed only by the rate of separation of the grips and is independent of, for example, the length of the tear.

The above features make this type of test-piece more convenient for the present investigation than most of those used for conventional tear resistance measurements.

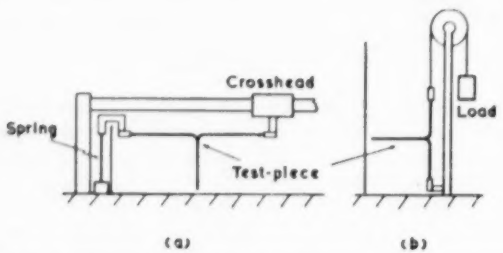


FIG. 2.—Methods of measurement: (a) constant rate of extension; (b) constant force.

Test-pieces with a width of 4 cm., a length of 10 to 15 cm., and a thickness of 1 to 2 mm. were normally used. The arms were formed by an initial cut of about 5 cm., and the tip of this cut, from which tearing was commenced, was formed with a razor blade. For test-pieces of these dimensions, the energy and rate of tear propagation may generally be derived with sufficient accuracy by the use of Equations (5) and (6). For vulcanizates that were highly tear resistant and extensible, however, corrections for the extension of the arms were made. The form of the corrections can be seen by a comparison of Equations (3) and (4) with (6) and (5), respectively.

Although the theoretical treatment of the test-piece assumes that the tear propagates along the central axis, it was found that in practice the measurements were not sensitive to small departures from this assumption.

METHODS OF MEASUREMENT

Two methods of measurement were employed, the first suitable for relatively high rates of tearing and the second for low rates. In the first and principal method, shown in Figure 2a, test-pieces were extended at various uniform rates in an extensometer. One arm of the test-piece was attached to the movable crosshead and the other to a calibrated cantilever spring. The crosshead was driven at constant speed by means of a motor and gear train, giving a continu-

ous range of speeds from 5×10^{-4} to 50 cm./sec., and the rate of tear propagation was derived from the crosshead speed by Equation (6). To determine the tearing force, and thereby the energy for tearing from Equation (5), the deflection of the spring was measured by means of an optical lever and scale. A spring, with a short period of the order of 0.01 second and approximately critically damped, was used.

In the second method, shown in Figure 2b, a constant tearing force was applied to a test-piece by means of weights, and the rate of tear propagation was measured. This was effected either by measuring, over a timed interval, the separation of the grips, using Equation (6), or by measuring directly on the test-piece the distance the tear had progressed in a timed interval. Rates of propagation from about 10^{-6} to 10^{-2} cm./sec. were determined by this method. When both methods could be applied, the range therefore extended from about 10^{-6} to 25 cm./sec.

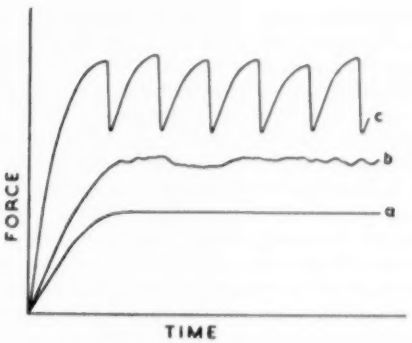


FIG. 3.—Schematic tearing force-time curves for constant rate of extension of the test-piece: (a) and (b) steady tearing; (c) stick-slip tearing.

The test-pieces were immersed during measurement in a water or alcohol thermostat controlled to $\pm 1°$ C, so that data could be obtained over a range of temperature. It was found from subsidiary experiments that immersion of the test-pieces in the liquids had no appreciable effect on the measurements.

TYPES OF TEARING

Although an examination of the torn surfaces of different vulcanizates would suggest that there are appreciable variations in the detail of the tear process, for measurement purposes tearing can be classified into two main types. These will be referred to as *steady and stick-slip*, respectively, and will be discussed initially in relation to the extensometer method of measurement, where the test-piece is extended at a uniform rate and the tearing force is observed. The difference between the two types of tearing is illustrated by the schematic force-time curves of Figure 3.

With steady tearing, the tearing force and rate of propagation remain essentially constant, apart from random fluctuations, once tearing has commenced. The fluctuations usually reflect the nature of the tear process. For example, when they are small (Figure 3a), the tear is generally straight and the torn surfaces are smooth in appearance to the eye; when they are appreciable

(Figure 3b), the path of the tear is tortuous and the torn surfaces are rough and irregular. For steady tearing conditions, the tear behavior is best represented by average values for the energy T and the rate of propagation, and these have been derived from the average tearing force and the crosshead speed, respectively. It is found, as would be expected, that T increases with the rate of propagation, i.e., the energy-rate relation has a positive gradient.

With the second type of tearing, a constant average rate of propagation can be maintained, but there are regular, as distinct from random, variations in the tearing force and rate of propagation. The tearing force fluctuates in a sequence consisting of a relatively slow increase to a maximum value and a more rapid decline to a minimum (Figure 3c), with corresponding variations in the rate of propagation. The fluctuations of the tearing force resemble the force fluctuations in certain frictional phenomena—hence the term stick-slip. As the crosshead speed is increased to give higher average rates of propagation, the maximum value of the tearing force diminishes until a point is reached where the tearing reverts to the steady type. Stick-slip tearing is clearly associated with an energy T which decreases with increasing rate of propagation, i.e., with an energy-rate relation of negative gradient, and the transition to steady tearing is associated with an energy minimum (see, for example, Figure 5). The appearance of the torn surface is again indicative of the nature of the tear process, the "stick" positions being marked, usually, by some surface irregularity.

For stick-slip tearing conditions, the tear behavior has been described in terms of the energy T, derived from the maximum tearing force, and the average rate of propagation, derived from the crosshead speed. The fluctuations of the rate of propagation are frequently large under stick-slip conditions, the rate falling virtually to zero at one point in the cycle. Under these circumstances, the use of the average rate of propagation provides a qualitative description of the dependence of the energy for tearing on the rate of propagation, but one which is nevertheless adequate for most purposes.

The constant force method of measurement cannot be used to determine the dependence of the energy T on the rate of propagation when the energy-rate relation has a negative gradient (*cf.* stick-slip in frictional phenomena). It has been used to extend the range of measurement when the relation has a positive gradient, i.e., under steady tearing conditions.

TEAR PROPERTIES OF GR-S AND NATURAL RUBBER GUM VULCANIZATES

EXPERIMENTAL RESULTS

The principal measurements, obtained at various temperatures in the range −20 to 90° C, refer to a natural rubber and a GR-S vulcanizate, each prepared by a conventional sulfur/accelerator cure. Other measurements to illustrate the effect of the degree of vulcanization were obtained with peroxide-cured vulcanizates. Details of the recipes and the times and temperatures of cure are given in the Appendix. The GR-S employed was Polysar-S, polymerized at 50° C, with 23.5 per cent bound styrene. The results are given in Figures 4 to 7 in the form of double logarithmic plots of the energy for tearing T, in ergs/cm.^{2}, as ordinate and the rate of propagation R, in cm./sec., as abscissa. Each plotted point represents the mean of several measurements on different test-pieces. The full and broken lines indicate steady and stick-slip tearing, respectively.

The tensile strength, elongation at break, and elastic constants C_1 and C_2 for the vulcanizates A to G, as listed in the Appendix, are given in Table I.

TABLE I

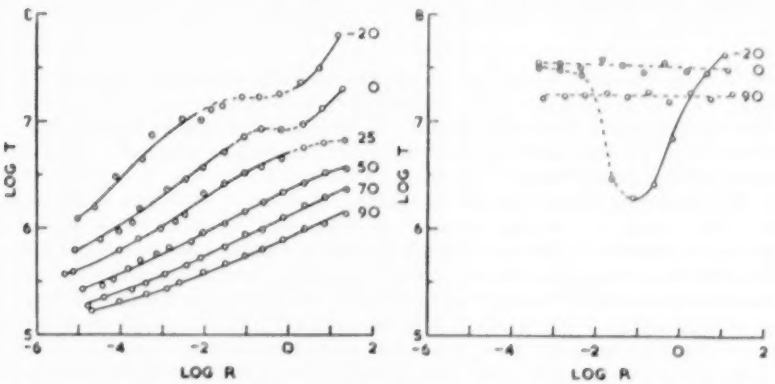
Vulcanizate	C_1 (kg./cm.²)	C_2 (kg./cm.²)	Tensile strength (kg./cm.²)	Elongation at break (%)
A (GR-S)	2.3	1.7	23	200
B (GR-S)	0.44	0.6	15	600
C (GR-S)	1.3	0.6	13	300
D (GR-S)	2.3	1.3	11	150
E (Natural rubber)	1.2	1.1	240	830
F (Natural rubber)	1.0	0.8	130	700
G (Natural rubber)	1.9	0.9	112	470

The tensile strength and elongation at break were measured at 20° C with a Goodbrand tensometer, and the elastic constants C_1 and C_2 were derived from simple extension stress-strain measurements by means of the relation:

$$f = 2A_0 (C_1 + \lambda^{-1}C_2)(\lambda - \lambda^{-2}) \qquad (7)$$

where f is the force, λ the extension ratio, and A_0 the undeformed cross-sectional area of the test-piece. Equation (7) adequately describes the stress-strain behavior of gum vulcanizates in simple extension in the region where the deformations are reversible[4]. The value of C_1 is used here as an approximate measure of the degree of vulcanization.

Results for the sulfur/accelerator cured GR-S vulcanizate A are given in Figure 4. Tearing is predominantly of the steady type, and it will be seen that the energy for tearing increases considerably with the rate of propagation. The effect of temperature is also considerable. At −20, 0, and 25° C, a limited amount of stick-slip tearing is observed, as indicated by the broken portions of the curves. Since the tear process in this type of vulcanizate is rather erratic in character, the rates of propagation at which the transitions from steady to stick-slip and from stick-slip to steady tearing occur are not well defined, and to preserve continuity in the measurements, the energy for tearing has been derived throughout from the average tearing force, regardless of any stick-slip behavior. The negative gradient associated with stick-slip tearing is, therefore, not obvious; nevertheless there are well-defined inflections in the curves at the lower



FIGS. 4. and 5.—Dependence of the energy for tearing T (in ergs/cm.²) on rate of propagation R (in cm./sec.) for the GR-S vulcanizate A (Fig. 4, left) and the natural rubber vulcanizate E (Fig. 5, right). The full and broken lines indicate steady and stick-slip tearing, respectively. The temperature, in ° C, is shown at each curve.

temperatures, separating two regions of steady tearing. The inflection coincides with a change in the torn surface from a rough, irregular appearance at low rates of propagation to a smoother one at high rates. It will be noted that the inflection occurs at higher rates of propagation as the temperature increases.

Figure 5 gives the results obtained with the sulfur/accelerator-cured natural rubber vulcanizate E. Tearing is predominantly of the stick-slip type. At $-20°$ C, the negative gradient associated with stick-slip tearing and the energy minimum at the transition to steady tearing are very pronounced. At temperatures from 0 to 90° C, there is also pronounced stick-slip tearing, but the precipitous decline of the energy T to a minimum value is not observed in the range of rates of propagation actually measured; it presumably occurs at some higher rate, as may otherwise be inferred from the very rapid decline of the tearing force during "slip". Evidently the energy minimum occurs at higher rates of propagation as the temperature increases, as with the inflections in the GR-S curves of Figure 4. Where the energy minimum associated with stick-

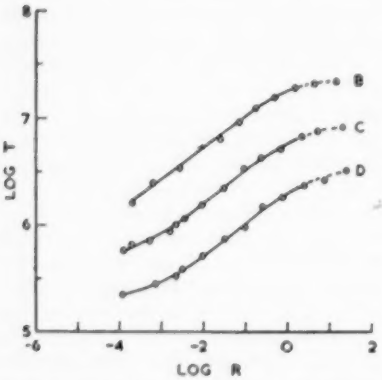


FIG. 6.—Dependence of the energy for tearing T (in ergs/cm.^{2}) on rate of propagation R (in cm./sec.) for the GR-S vulcanizates B, C, and D at 25° C.

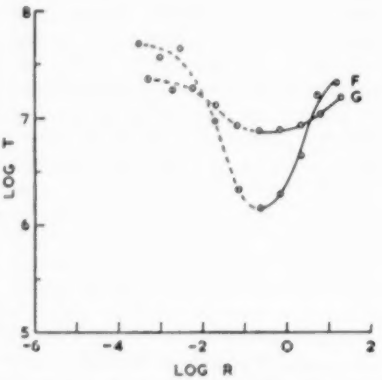


FIG. 7.—Dependence of the energy for tearing T (in ergs/cm.^{2}) on rate of propagation R (in cm./sec.) for the natural rubber vulcanizates F and G at $-20°$ C.

slip tearing does not occur in the range of measured rates of propagation, the value of T at the minimum can be estimated from the force minima during stick-slip. At 0 and 90° C, it appears that this minimum value is less by a factor of about 2 than the value of T at low rates of propagation, and at $-20°$ C, as may be seen directly from Figure 5, the factor is about 16.

The curves of Figure 5 indicate that, for sufficiently low rates of propagation, the energy for tearing attains a substantially constant value T_ϵ, for a given temperature. Tests were made in which a static load was applied to a partially torn test-piece and, when the load was applied reasonably slowly, no continuous growth of the tear was observed, unless the load was sufficient to provide an energy for tearing of about the value T_ϵ. It was estimated that a rate of propagation as low as 10^{-3} cm./sec. would have been perceptible. Hence T_ϵ represents, in practice, a critical or limiting energy below which continuous tearing is not observed, unless the test-piece is extended comparatively rapidly.

Comparing the two vulcanizates A and E of Figures 4 and 5, it will be observed that for low rates of propagation the value of T for the GR-S is consider-

ably lower than that for the natural rubber, and with the GR-S there is little evidence of a limiting energy for tearing. At high rates of propagation and low temperatures, however, the value of T is of a similar order for both. It will also be noted that, at the lower temperatures, both stick-slip and steady tearing are observed with each vulcanizate.

The effects of the degree of vulcanization on tear properties are illustrated in Figures 6 and 7. The results given in Figure 6 were obtained at 25° C, and refer to the peroxide-cured GR-S vulcanizates B, C, and D. As would be expected from the trend of the tensile strength and elongation at break values of Table I, increasing vulcanization (increasing C_1) decreases the energy for tearing, although the form of the curves remains substantially unchanged. The results of Figure 7 refer to the peroxide-cured natural rubber vulcanizates F and G, and were obtained at −20° C. Here the effects are rather more complex. Stick-slip tearing becomes less pronounced and the critical energy for tearing T_c (the limiting value of T at low rates) is evidently reduced by increasing vulcanization. Under steady tearing conditions at high rates of propagation, the energy T is also somewhat reduced by increasing vulcanization.

DISCUSSION

The conventional single tear resistance value has been replaced, in the present method of characterizing tear properties, by experimental curves showing the dependence of the energy for tearing on the rate of propagation. A single value for the tear resistance may be useful in cases where there is a well-defined limiting energy for tearing, but the experimental results show that it is not a complete description; in other cases a single value is inadequate. The present method is an appropriate one for an investigation of the tear process, and the experimental results indicate that the tear process and the tear resistance can change with the rate of propagation and the temperature.

The experimental results may alternatively be presented in terms of the dependence of the energy for tearing T on the rate of extension of the test-piece, and from this it is possible to assess the change of tear resistance which occurs when the force applied to a test-piece is increased either slowly or rapidly. For example, with natural rubber gum vulcanizates the tear resistance, as represented by the energy T, is high for low rates of increase of the applied force; at higher rates it is lower, and at still higher rates it again becomes high. In contrast, the tear resistance of GR-S gum vulcanizates is low for low rates of increase of the applied force and is high for high rates.

Comparison of the results obtained with natural rubber and GR-S vulcanizates shows that under suitable conditions both can exhibit steady or stick-slip tear behavior. Thus it appears that the differences between these vulcanizates are ones of magnitude and of characteristic rates and temperatures rather than of any fundamentally different behavior.

As mentioned, stick-slip behavior is indicative of a negative gradient in the energy-rate of propagation relation. This is presumably associated with the presence at the tip of the tear of a strengthening structure that takes an appreciable time to form, the time required being dependent (*inter alia*) on the temperature. In the case of gum vulcanizates, it seems plausible to identify this structure with crystallization, or something akin to it, produced by the high extension of the rubber in the neighborhood of the tip of the tear. With peroxide-cured natural rubber vulcanizates, which are transparent, there is visible evidence of crystallization, under stick-slip tearing conditions, in the opacity

developed at the tip of the tear. The effect of this strengthening structure on the tear properties of GR-S vulcanizates is small, but perceptible. Presumably this type of vulcanizate may crystallize to a slight extent on stretching. It is interesting to note that there is other evidence, derived from stress relaxation measurements, that GR-S vulcanizates may show, to some extent, features similar to crystallization[5]. We should expect stick-slip behavior and a negative gradient in the energy-rate of propagation relation, where there is a decrease of the amount of the strengthening structure with increasing rate of propagation. We should not expect this behavior at high rates of propagation with low temperatures, where there is insufficient time for the structure to form, and the experimental results bear out this view.

The description of certain features of tearing in terms of a strengthening structure, such as crystallization, implies that secondary forces between the rubber molecules may considerably influence the tear properties. This is also indicated by the effect of swelling and by a comparison of GR-S with a butadiene-styrene copolymer of high styrene content. Thus, if a GR-S vulcanizate is swollen to twice its original voulme, the value of T at a particular rate of propagation is reduced by a factor of about 4; and for a vulcanizate with a 50 per cent styrene content, the value of T at a particular rate of propagation may be increased by a factor of about 10 in comparison with GR-S.

The variation of the energy for tearing T with the rate of propagation reinforces the statement already made that T is to be interpreted as the energy expended irreversibly in tearing. It has been shown by the author[2] how this irreversible expenditure of energy may be ascribed to the extension and rupture of the rubber in the immediate neighborhood of the tip of a tear, and that T is given in order of magnitude by the relation:

$$T \approx d\,E \tag{8}$$

where d is the effective diameter of the tip of the tear and E is the work to break/unit volume in simple extension for the rubber. At the tip of the tear the rubber is in simple extension. In general, we may expect E to vary with the rate of extension entailed in its measurement, and the rate of extension of the rubber in the neighborhood of the tip of the tear will depend on the rate of propagation. Thus, from Equation (8), we may expect T and E to vary in a qualitatively similar manner with the rate of tear propagation and the rate of extension, respectively, for conditions, such as steady tearing, where d is likely to be constant. The data of Dogadkin and Sandomirskiĭ[6] and of Villars[7], concerning the variation of tensile strength and elongation of break with rate of extension suggest that this expectation may well be true.

It has also been shown by the author[2] that, for a natural rubber vulcanizate, the effective diameter d of the tip of the tear, as derived from Equation (8), is of the order of 10^{-2} cm. and, as might be expected, the irregularities in the torn surface are of a similar order. It has been observed that, in passing from stick-slip to steady tearing with increasing rate of propagation, the torn surface becomes smoother, which suggests that there may be a corresponding decrease of d. This variation of d in the stick-slip region would tend to enhance the effect on T of any decrease in E with rate of extension.

SYNOPSIS

A method of investigating the tear behavior of rubber vulcanizates is described. The method, based on the tear criterion of Rivlin and Thomas, in-

volves the determination of the energy required to propagate a tear and its dependence on the rate of propagation. The type of test-piece employed and the methods of measuring the energy and rate of tear propagation are described and discussed. Two principal types of tearing, indicative of different tear processes, are described. Experimental results for natural rubber and GR-S gum vulcanizates, obtained over a wide range of temperature and rate of propagation, are given to illustrate the method. The results indicate that the nature of the tear process and the resistance to tearing, as represented by the energy required to propagate a tear, can change appreciably with the rate of propagation and the temperature. The significance of these changes is discussed.

APPENDIX

The compounding details of the vulcanizates used in this investigation were as follows.

Vulcanizate	A	B	C	D	E	F	G
GR-S (Polysar-S)	100	100	100	100	—	—	—
Natural rubber (smoked sheet)	—	—	—	—	100	100	100
Sulfur	3	—	—	—	3	—	—
Zinc oxide	5	—	—	—	5	—	—
Stearic acid	1	—	—	—	1	—	—
Mercaptobenzothiazole	1	—	—	—	0.5	—	—
Diphenylguanidine	0.5	—	—	—	—	—	—
Antioxidant	0.5	—	—	—	1	—	—
2,2-Di-(*tert*-butylperoxy) butane	—	1	3	9	—	1	3
Time of cure at 140° C (min.)	40	45	45	150	45	30	30

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THE KINETICS OF HIGH-ELASTIC DEFORMATION*

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It is generally known that in the isothermal deformation of an elastic body, a very considerable amount of time is sometimes required for reaching an equilibrium ratio between the parameters of state (deformation and stress).

In 1867 Maxwell proposed a rather simple theory of the mechanical properties of a body, in which the stress brought about during deformation depended, not only on the extent of the deformation (as in solid bodies which obey Hooke's law), but also on the speed of this (as in liquids which obey the Newton law of viscous flow). The mechanical properties of Maxwell's elastic-viscous body may be described by the simple differential equation:

$$\frac{d\sigma}{dt} = E_0 \cdot \frac{d\epsilon}{dt} - \frac{\sigma}{\tau} \qquad (1)$$

The latter relates the deformation ϵ, the stress σ and the time t, and it contains two constants: the modulus E_0, characterizing the elastic properties of a body, and the time of relaxation τ, which characterizes the viscous properties of the system.

The physical significance of τ can be interpreted in two way. In the case of a constant deformation stress, $\left(\frac{d\sigma}{dt} = 0\right)$, the time of relaxation is proportional to the coefficient of viscosity in the Newton equation for viscous flow ($E_0\tau = \eta$). However, in the case of constancy of deformation, $\left(\frac{d\epsilon}{dt} = 0\right)$, this quantity is the reciprocal of the constant of speed for the process of relaxation of the stress, which is described by the equation of a first-order reaction, $\left(-\frac{d\sigma}{dt} = \frac{1}{\tau} \cdot \sigma\right)$.

The Maxwell theory gives a good qualitative description of the mechanical behavior of systems which exhibit the ability to undergo irreversible (plastic) deformation. A quantitative verification, however, reveals marked discrepancies between theory and experiment. This is the reason why, in order to describe the relaxation process, we proposed, in place of the ratio in Equation (1), some other equations which have, however, only an empirical nature. In particular, Gurevich assumed τ in Equation (1) to be a quantity which depends not only on the temperature, but also on the stress. Maxwell himself had expressed thoughts as to the possible existence of such a dependence. In a very general way, this hypothesis was confirmed by Aleksandrov[1]. Gurevich[2] does not attempt to give the theoretical basis for this relationship, but postulates

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it in the form of this expression:

$$\tau = \tau_0 \cdot e^{\frac{u_0 - a \cdot \sigma}{KT}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where τ_0 is a constant which does not depend on temperature and stress; u_0 is the activation energy; and a is an empirical constant.

Without dwelling in detail on the work of the latter author, we may note only that the successful application of the relation in (2) by Gurevich in representing the deformation of the materials studied by him (for the case of stress with constant speed), gives a basis for the idea that the time of relaxation τ in the Maxwell equation is a function of the stress σ, and that this is an entirely correct and useful idea.

In fact, according to our presentation, the relaxation of stresses in polymers within the time limits studied is substantially a process of rearranging the intermolecular bonds, with a mutual displacement of the structural elements in the chains. The presence of a condition of stress should speed up processes of this type. At the same time we conceive of stress relaxation as a combination of two processes: (1) separately occurring acts of rearrangement of the separate structural elements of the chain, and (2) a continual equalizing of the stresses as a result of mechanical reaction between these elements. As a consequence of the latter process, a gradual lessening of the tension takes place in those elements which have not yet taken part in acts of relaxation, which slows down the first process and, as a result, leads to an increase of the relaxation time in the operation of the process in question.

Turning to Equation (2), however, we are compelled to reject it purely from a consideration of its form. Actually, according to the equation, τ is an odd function of stress. But this means that, for example, in the case of shear stress, a change in the direction of the action of the force should change the numerical value of the time of relaxation. It is plain that, in seeking the function between the time of relaxation and the stress, one should note the requirement for an even function. An attempt to reach a theoretical conclusion as to the dependence of relaxation time on stress was undertaken on the basis of interpreting τ as a kinetic constant in a process described by an equation for a first-order reaction. Actually, for the individual case of the relaxation of a stress where the length is constant, we derive from Equation (1) the following:

$$\frac{d\sigma}{dt} = \frac{1}{\tau} \cdot \sigma \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The expression (3) coincides, in its form, with the equation of a first-order reaction, in which τ emerges as a quantity which is the reciprocal of the speed constant. Hence a fair approximation of the process being studied would be found in an equation analogous to the Arrhenius equation:

$$\tau = \tau_0 \cdot e^{\frac{u}{KT}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

which was proposed by Aleksandrov[1] in particular. An indispensable condition for the application of Equation (4) in the process of stress relaxation under study, however, is the requirement that any change in the energy of the initial state during the operation of the process is limited by the change in the number of strained elements of structure, under a constant tension.

Actually this requirement does not obtain in our case, since the structural

elements which go to make up the sample are found to react together mechanically to some extent. An individual act of relaxation taking place in one of the elements of structure brings about, through this interreaction, some reduction of the stress in the surrounding elements which have not yet participated in the act of relaxation, and thus the energy level of the initial state is continually being lowered. This lowering causes the energy of activation u in Equation (4), which is considered to be the difference between the energies of the activated and the initial state, to increase in the course of the relaxation process up to a certain value u_0 which is characteristic of the equilibrium that is established. The increase of the activation energy, which is equal to the reduction in the energy of the initial state, is determined approximately by the energy which is dissipated in the course of the process and equals the loss of

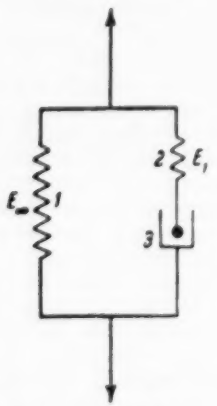

FIG. 1.—(No caption given; this is a diagram of the mechanical model, as described in the text.)

elastic energy during relaxation. Designating the momentary value for the activation energy (with respect to the kinetic element of relaxation) by u, and the elastic energy for the same element by w, we get:

$$du = -dw \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

For a mechanical model to represent the relaxation properties of high-elasticity materials, we may adopt one of the simples kinds of models, as depicted in Figure 1. This is seen to be a parallel coupling of a spring, *1*, with a mechanical element formed by a connection in series of the spring, *2*, and the viscous element (damper), *3*. The equilibrium value for stress in this model depends on the deformation of the spring, *1*, which possesses the modulus E_∞. An excess stress value, corresponding to a system not in a state of equilibrium, depends on the deformation of the spring, *2*, with a modulus of E_1. The speed of the relaxation of stresses is determined, in this model, by the properties of the viscous element, *3*, since the constant τ which we considered earlier is now proportional to the viscosity of this element.

However, we should avoid drawing too close an analogy between the model studied and the actual structure of a polymer. The differential equation expressing the law of deformation for the model in Figure 1 is analogous to the

Maxwell equation, and takes the form:

$$\frac{d(\sigma - \sigma_\infty)}{dt} = E_1 \cdot \frac{d\epsilon}{dt} - \frac{\sigma - \sigma_\infty}{\tau} \quad (6)$$

where

$$\sigma - \sigma_\infty = \sigma - E_\infty \cdot \epsilon = \sigma_1 \quad (7)$$

It should be noted that the model proposed, while giving a good qualitative description of the behavior of polymers, leads to a distinctly incongruous one, quantitatively, if the time of reaction τ is not assumed to depend on the stress.

As one of us showed[3], one may adopt as a law of deformation for non-crystallizing polymers Hooke's law, which has been confirmed experimentally within a broad range of deformation. Taking the Poisson coefficient as 0.5 (which is reasonable for the majority of polymers), it is easy to derive an expression for the quantity of the elastic energy, as a function of the deformation of spring *2* in our proposed model (Figure 1):

$$W_{\text{spec.}} = \sigma_1 - E_1 \log\left(\frac{\sigma_1}{E_1} + 1\right) \quad (8)$$

Solving by series and using only the first term, we get:

$$W_{\text{spec.}} \approx \frac{\sigma_1^2}{2E_1} \quad (9)$$

In order to make a substitution in Equation (5), we must relate the energy to the volume occupied by the "kinetic element of relaxation". Designating the latter by v, we get:

$$W = W_{\text{spec.}} \cdot v = \frac{v \cdot \sigma_1^2}{2E_1} \quad (10)$$

Substituting the value obtained in Equation (5) and differentiating with the assumption that v does not change in the relaxation process, we get:

$$du = -\frac{v \cdot \sigma_1 \cdot d\sigma_1}{E_1} \quad (11)$$

Using the designation u_0 for the activation energy of the elementary transformation (a component of the relaxation mechanism)in the absence of an excess of stress ($\sigma_1 = 0$), one may integrate with a substitution of the corresponding limits. Since

$$\int_{u_0}^{u} du = -\frac{v}{E_1} \int_0^{\sigma_1} \sigma_1 \cdot d\sigma_1 \quad (12)$$

then after integration and substitution of the value σ_1 from the Equation (7), we get:

$$u = u_0 - \frac{v}{2E_1}(\sigma - \sigma_\infty)^2 \quad (13)$$

From this, making use of Equation (4), we have:

$$\tau = \tau_0 \cdot e^{\frac{u_0 - \frac{v}{2E_1}(\sigma - \sigma_\infty)^2}{KT}} \quad (14)$$

The expressions derived are different from Equation (2) in that τ is an even function of the stress, and is free of the incongruity by reason of which we found Equation (2) unsuitable. Further, in place of the empirical constant a in Equation (2), we have here a coefficient in $(\sigma - \sigma_\infty)^2$ which possesses a definite physical significance. Of special interest is the fact that the volume of the kinetic element of relaxation enters into Equation (14); since when this is not known, our concept of activation energy always remains somewhat indefinite by reason of the fact that we do not know what sort of dimensions this element, on which the energy value should depend, may have.

From Equation (6), for the case of relaxation of stress when the length is constant $\left(\frac{d\epsilon}{dt} = 0\right)$ we get:

$$-\frac{d\sigma}{dt} = \frac{1}{\tau}(\sigma - \sigma_\infty) \qquad (15)$$

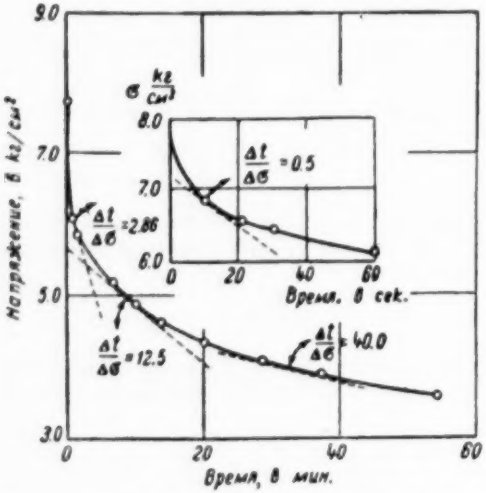

FIG. 2.—Stress relaxation in a film of smoked sheet at an elongation of 100% and a temperature of 22° C. The abscissa of the outer square represents relaxation time in minutes, that of the inner figure time in seconds; both ordinates represent stress in kg. per sq. cm.

The latter expression, in conjunction with Equation (14), gives the differential law of relaxation for rubberlike polymers.

The differential equation obtained when Equation (14) is substituted in Equation (15) is not integrated in the final form. Solving by series, we may get a solution with any desired degree of accuracy; however, for an experimental verification of the theory, we employed the differential law directly, having recourse to the method of finite differences for analyzing the experimental curves.

We verified the applicability of the concepts developed here for the case of several rubberlike polymers, investigating the relaxation of stresses at various temperatures and elongations.

The stress-relaxation curves were obtained from measurements made with a precision dynamometer which was constructed especially for our problem by the

TABLE 1

CHANGE OF THE RELAXATION TIME τ IN THE PROCESS OF STRESS RELAXATION. FILM OF NATURAL RUBBER (SMOKED SHEET) (ELONGATION 100%; TEMPERATURE 22° C)

t	$\sigma - \sigma_\infty$	$\frac{\Delta t}{\Delta \sigma}$	τ	$\log \tau$
10 sec.	7.0	0.5	3.5	0.542
1 min.	6.0	2.86	17.16	1.234
8 min.	5.0	12.5	62.5	1.796
32 min.	4.0	40.0	160.0	2.204

laboratory apparatus works of the Mendeleev M.O.V.Kh.O., and is now in widespread use.

Figure 2 shows a typical stress-relaxation curve for natural rubber (smoked sheet), which was tested in the form of a film deposited on the surface of cellophane by evaporation of the solvent (benzene) from a rubber solution.

From Equation (15) we get:

$$\tau \approx -\frac{\Delta t}{\Delta \sigma}(\sigma - \sigma_\infty) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$

where σ_∞ is the equilibrium value for the stress which corresponds to a given elongation and temperature. We determined this quantity on the dynamometer mentioned above, by a method which is analogous to the method of Meyer and Ferri[4].

In the case of unvulcanized films of natural rubber the equilibrium stress σ_∞ is close to zero. Knowing σ_∞ we may, determine from Figure 2 the momentary values of τ at various points corresponding to the values of the difference

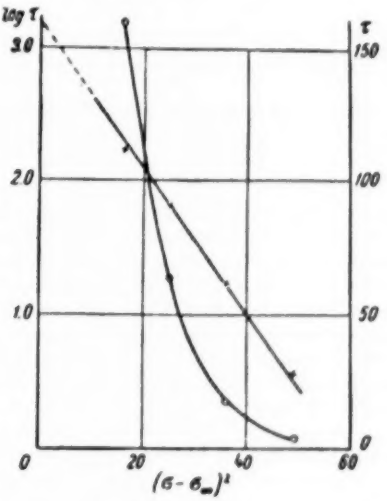

FIG. 3.—The relation of τ as calculated in the equation $\tau = -(\sigma - \sigma_\infty)\frac{\Delta t}{\Delta \sigma}$ for stress in excess of the equilibrium stress (plotted on linear and semilogarithmic coordinates).
o-o-o—$\tau = \varphi[(\sigma - \sigma_\infty)^2]$.
x-x-x—$\log \tau = \varphi[(\sigma - \sigma_\infty)^2]$.

$\sigma - \sigma_\infty$. It can be seen from Figure 2 and the data of Table I how this value changes in the course of the process.

Furthermore, the correctness of Equation (14) can be verified by plotting these experimentally found values of τ with respect to $(\sigma - \sigma_\infty)^2$. For this it is convenient to use a semilogarithmic scale, since a logarithmic treatment of Equation (14) gives

$$\log \tau = \log \tau_0 + \frac{u_0}{KT} - \frac{v}{2E_1 KT}(\sigma - \sigma_\infty)^2 \quad \ldots\ldots\ldots\ldots (17)$$

where ln τ is a linear function of $(\sigma - \sigma_\infty)^2$. Figure 3 shows that the experimentally derived values for log τ, plotted against $(\sigma - \sigma_\infty)^2$, actually fall nicely on the straight line drawn to represent log τ versus $(\sigma - \sigma_\infty)^2$.

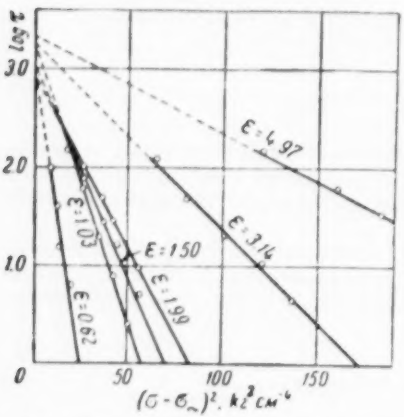

FIG. 4.—Relation between relaxation time and stress in excess of the equilibrium stress, at various elongations (smoked sheet) at a temperature of 22.5° C. The abscissa represents this excess stress in kg per sq. cm. (squared).

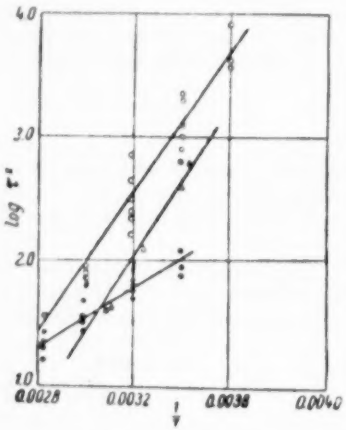

FIG. 5.—Relation between the limiting value for relaxation time, τ^*, and the temperature. ○—Smoked sheet; ●—Brominated rubber; △—Buna S-3.

As was already shown, we investigated various types of rubberlike polymers, and in all cases we found a good agreement between theory and experiment. Discrepancies, which apparently were due to the superimposed crystallization effect, were noted only in the case of natural rubber at elongations in excess of 300 per cent and at temperatures below 0° C.

Of decided interest is the determination of the activation energy u_0 in the relaxation process which we are studying. For this purpose, designating the limiting value of the relaxation time as τ^*, when $(\sigma - \sigma_\infty) \to 0$, we get the following from Equation (17):

$$\log \tau^* = \log \tau_0 + \frac{u_0}{KT} \quad \ldots\ldots\ldots\ldots\ldots\ldots (18)$$

Figure 4 shows the experimental straight lines obtained for natural rubber when stress relaxation is investigated for various elongations. Here the segments which the straight lines intersect on the ordinate axis are numerically equal to the various values of log τ^*.

If we plot τ^* against $\frac{1}{T}$, then according to Equation (18) we should expect a linear relation. A similar approach to linearity is found in natural rubber, as well as in a vulcanizate of butadiene-styrene rubber (Buna-S), and this is also found in brominated rubber, which we investigated specially. The slope of the straight lines of Figure 5 permits a direct calculation of the activation energy which corresponds to a zero value for $\sigma - \sigma_\infty$. The calculation yields a value of the order of 15–17 kcal. for both smoked sheet and butadiene-styrene rubber. As was noted earlier, the activation energy is related to a conditional gram-molecule, where "molecule" means the "kinetic element of relaxation". It has been found possible to determine the volume of this kinetic element of relaxation v. The latter can be determined from the slopes of the straight lines in Figures 3 and 4, since, according to Equation (17):

$$2.3 \tan \varphi = \frac{v}{2E_1 KT} \qquad (19)$$

Now a direct determination of v from this equation requires that we know the quantity E_1; we may, however, obtain the latter directly by experiment. Some idea of the value of this quantity may be gained from curves of deformation against stress, achieved with a constant speed of deformation.

For this case, when $\frac{d\epsilon}{dt}$ is constant, then by way of Equation (6) we may arrive at the equation:

$$\frac{d\sigma}{d\epsilon} = (E_1 + E_\infty) - \frac{\sigma - \sigma_\infty}{\tau \cdot \frac{d\epsilon}{dt}} \qquad (20)$$

From this it follows immediately that $E = E_1 + E_\infty$ is determined by the tangent of the angle of the slope which is tangential to the curve of $\sigma = \varphi(\epsilon)$ where $\epsilon \to 0$.

Having thus determined the approximate value of E_1 and substituted this in Equation (19), we were able to calculate the volume of the kinetic element of relaxation v. As can be seen from the graphs in Figure 4, this quantity depends greatly on the deformation. For natural rubber at 22° and 100 per cent elongation it amounts to 160,000 cu. Å. The quantity derived here is of the same order of magnitude as the volume of the kinetic element of fluidity (352,000 cu. Å), as calculated by Smallwood from the viscosity of unvulcanized rubber. From our viewpoint this agreement bears witness to the fact that the molecular mechanism of the stress relaxation phenomenon which we have studied and the mechanism of viscous flow are closely related in their nature.

Without departing, in the present communication, from the frame of reference of the task of giving a detailed account and discussion of the experimental data which we obtained, we may point out only that Equation (14) which we propose embraces the constants which appear to determine completely the relaxation properties of the polymers for the given parameters of state and for the periods of observation adopted. The clarification of the dependence of these constants (v, τ, E) on temperature is, in our opinion, of considerable interest from the standpoint of revealing the mechanisms of such phenomena as vitrification, crystallization, fluidity at high temperatures, and other peculiarities of high-elastic polymers.

CONCLUSIONS

1. The following equation is proposed:

$$\tau = \tau_0 \cdot e^{\frac{u_0 - \frac{v}{2E_1}(\sigma - \sigma_\infty)^2}{KT}}$$

to relate the time of relaxation τ to the value for excess stress, $\sigma - \sigma_\infty$. In combination with the expression:

$$-\frac{d\sigma}{dt} = \frac{1}{\tau}(\sigma - \sigma_\infty)$$

it gives the differential law of relaxation for rubberlike materials.

2. The physical significance of the constants (u_0, v, E_1) which enter into this equation is revealed, and a method is given for determining these values experimentally from the curves of stress relaxation at a constant deformation and from curves of deformation versus stress at a constant speed.

3. With natural rubber and vulcanizates of butadiene-styrene rubber as examples, it is shown that the equations introduced, which differ from the usual form of the Maxwell equation, agree quantitatively with experimental data.

4. The values calculated for the activation energy, u_0, of the rubbers mentioned lie in the range of 15–17 kcal./mole, while the calculated volume of the kinetic element of relaxation v at a temperature of 22° C, and an elongation of 100 per cent amounts to about 160,000 cubic Å.

5. Opinions are expressed concerning the significance of the hypothesis developed to show a relation between the relaxation characteristics of a polymer and the temperature range in which it exhibits high-elastic properties.

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THEORY OF TWO-DIMENSIONAL STRETCHING OF RUBBER *

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Equilibrium two-dimensional deformation of the spatial network of rubber has been discussed in other works[1]. Treloar proposed the following relation for uniform two-dimensional stretching[2], with equal main stresses:

$$\sigma_1 = \sigma_2 = \sigma: \quad t = G(1 - \alpha^3) \tag{1}$$

where t is the tension, equal to the stress per unit area of the cross-section of stretched sheet and unit initial thickness; α is the relative thickness, equal to the ratio d/d_0, where d_0 and d represent the thickness of the rubber sheet before and after stretching; and G is the shear modulus.

Since an elastic material such as rubber shows high final deformations, it is necessary to take into consideration the relative stretching λ. This value is the ratio of a linear unit in the plane of stretching after deformation to its corresponding dimension before stretching. The relative stretching is related to the deformation and stresses by the following equations:

$$\lambda = 1 + \epsilon \quad \text{where} \quad \epsilon = \epsilon_1 = \epsilon_2 \quad \text{and} \quad \sigma = \lambda f = \lambda^3 t \tag{a}$$

where f is the conventional and σ the true stress. Discounting the condition of incompressibility: $\alpha \cdot \lambda^2 = 1$, formula (1) can be transformed into:

$$\sigma = G\left(\lambda^2 - \frac{1}{\lambda^4}\right) \tag{2}$$

From the formula for the elastic potential proposed by Wall, Treloar and others, the following relation besides Equation (2), can be derived for the one-dimensional stretching of rubber:

$$\sigma = G\left(\lambda^2 - \frac{1}{\lambda}\right) \tag{3}$$

At medium and high deformations, this relation shows deviations from the experimental data[3]. Figures 1 to 4 show that this also applies to two-dimensional stretching. The equation of uniaxial deformation, derived on the basis of orientation theory[4] agrees better with the experimental data[5] in the whole range of stretching.

We shall consider the isothermic equilibrium two-dimensional stretching of 1 cc. of rubber, starting with the orientation theory of high elastic deformation. The external deforming forces, $F_1 = F_2 = F$, are applied in this case to 1 sq. cm. of the surface of corresponding sides taken before deformation, and for this reason are numerically equal to the conventional stress f.

* Translated for Rubber Chemistry and Technology from the *Kolloidnyi Zhurnal*, Vol. 17, No. 1, pages 18–23 (1955).

Two-dimensional stretching from a macroscopic standpoint is uniform in any direction in the plane of stretching. From the molecular point of view, the mechanism of stretching of the separate chains is not homogeneous. In the direction chosen, the chains are deformed at various angles, since stretching of the separate chains is equally probable in all directions of the plane of two-dimensional stretching. For a chain stretched by the action of elementary stresses applied to its ends (cross-links of the chain network), the same considerations are, in general, applicable as for a chain stretched unidimensionally. The greater is the two-dimensional stretching of a chain which is highly entangled in the undeformed state, the more valid this assumption becomes. The distance between the ends of a chain, according to[4] is equal to $zlL(x)$ where L is the Langevin function from the argument $x = \omega + \frac{p \cdot \sigma}{k \cdot T}$; z is the number of segments in the chain ($z \gg 1$); l is the length of a segment; ω and p are constants of the rubber.

In the structure of rubber, two chains are necessary for every cross-link[6]. Consequently, $N/2$ cross-links are necessary for N chains in 1 cc. The number of chains necessary for 1 cm. of the edge of an undeformed cube is roughly equal to the number of cross-links necessary for the same side. This number is equal to $(N/2)^{\frac{1}{3}}$.

In the deformed state, the length of the edges in the plane of two-dimensional stretching, numerically equal to λ, can be determined as the sum of projections on these edges of $(N/2)^{\frac{1}{3}}$ deformed chains oriented in all directions.

Hence:

$$\lambda = zl \left(\frac{N}{2}\right)^{\frac{1}{3}} L(x) \overline{\cos \varphi} \tag{b}$$

where:

$$\overline{\cos \varphi} = \frac{1}{\pi} \int_{-\pi/2}^{+\pi/2} \cos \varphi \, d\varphi = \frac{2}{\pi} \tag{c}$$

replacing x and $\cos \varphi$ by their values, we obtain:

$$\lambda = \frac{2}{\pi} zl \left(\frac{N}{2}\right)^{\frac{1}{3}} L\left(\omega + \frac{p\sigma}{kT}\right) \tag{4}$$

When $\sigma = \infty$, the relative elongation theoretically reaches a maximum value $\lambda_\infty = \lambda_\infty^{(2)}$, and $L = 1$. It follows that:

$$\lambda_\infty^{(2)} = \frac{2}{\pi} zl \left(\frac{N}{2}\right)^{\frac{1}{3}} \tag{d}$$

Thus, the maximum relative elongation $\lambda_\infty^{(2)}$ during two-dimensional stretching is $\pi/2$ times smaller than the maximum relative elongation $\lambda_\infty^{(1)}$ during one-dimensional stretching.

Placing $\sigma = 0$ and $\lambda = 1$ in Equation (4), we obtain[7] $\omega = L_* \left(\frac{1}{\lambda_\infty^{(2)}}\right)$

Utilizing this, instead of formula (4) we have:

$$\sigma = \frac{kT}{p} \left\{ L_* \left(\frac{\lambda}{\lambda_\infty}\right) - L\left(\frac{1}{\lambda_\infty}\right) \right\} \tag{5}$$

The equation obtained is valid also for one-dimensional deformation, if λ and $\lambda_\infty = \lambda_\infty^{(1)}$ represent values corresponding to uniaxial stretching. For thin

spatial networks where λ_∞ is large, Equation (5) can be simplified to a linear approximation for the series:

$$L_*\left(\frac{\lambda}{\lambda_\infty}\right) = L_*\left(\frac{1}{\lambda_\infty}\right) + L'_*\left(\frac{1}{\lambda_\infty}\right)\frac{\lambda - 1}{\lambda_\infty} + \cdots$$

For unloaded low-modulus rubbers, this substitution is true up to 100–200 per cent deformation with an accuracy of several per cent. Hence we obtain for one- and two-dimensional stretching the following approximate equations:

$$\sigma = E(\lambda - 1) = E\epsilon; \quad \sigma = D(\lambda - 1) = D\epsilon \tag{6}$$

where the moduli of uni- and two-dimensional stretching are:

$$E = \frac{kT}{p\lambda_\infty^{(1)}} L'_*\left(\frac{1}{\lambda_\infty^{(1)}}\right); \quad D = \frac{kT}{p\lambda_\infty^{(2)}} L'_*\left(\frac{1}{\lambda_\infty^{(2)}}\right) \tag{7}$$

Since $\lambda_\infty^{(1)} = \frac{\pi}{2}\cdot\lambda_\infty^{(2)}$, we find the relation between the moduli:

$$\frac{D}{E} = \chi\frac{\pi}{2} \tag{8}$$

where

$$\chi = L'_*\left(\frac{1}{\lambda_\infty^{(2)}}\right) \Big/ L'_*\left(\frac{1}{\lambda_\infty^{(1)}}\right)$$

In the case of spatial networks of the lowest density, $\chi = 1$.

Data obtained by N. M. Novikova for one- and two-dimensional stretching of unloaded butadiene-styrene rubber (Buna-S) are shown in Figures 1 and 2. The data were obtained on specimens from one piece of vulcanized rubber, and each point on the graphs represents an individual specimen. Equilibrium was reached by relaxation of stress at 70° by a method described earlier[4]. In Figures 3 and 4 are presented Treloar's data[5] for unloaded vulcanized natural rubber.

In comparing the theory with the experiment, we shall first consider small deformations, for which the classic theory of elasticity is valid, and there is almost no difference between the true and conventional stress. For a strict confirmation of the formulas of two-dimensional deformation, it is necessary to determine the constants in these formulas from other independent experiments. Such are determinations of the modulus of one-dimensional stretching E (line 5 in Figure 1) and the determination of $\lambda_\infty^{(1)}$ (from the tensile strength characteristics of rubbers containing an active filler, as is shown in Figure 5), both carried out by the authors for synthetic rubber. The method of determining the maximum relative stretching differs from that proposed earlier for natural rubber[4] in that extrapolation is used instead of a direct measurement (Figure 5), requiring no additional interpretation. The values obtained are: $E = 12.0$ kg./cm.^{2} and $\lambda_\infty^{(1)} = 10.2$; hence, $\lambda^{(2)} = 6.5$, $\chi = 1.025$; $k\cdot T/p = 40_\infty$, 1 kg./cm.^{2}.

Formulas (2) and (3) at small deformations (a few per cent) become the formulas of the theory of elasticity for incompressible isotropic materials, according to which the following relations hold between the moduli: $E = 3G$ and $D = 2E$. Accordingly it is necessary to substitute the shear modulus $G = 4.0$ kg./cm.^{2} in these equations.

Figure 1 gives the theoretical relations, from which it follows that Treloar's

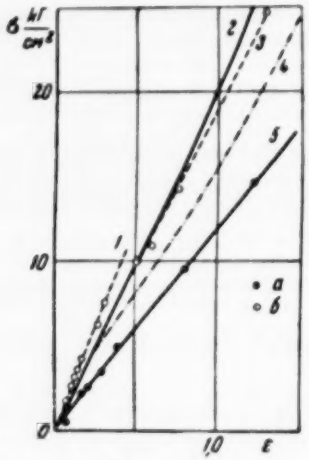

FIG. 1.—Data on (a) one-dimensional and (b) two-dimensional stretching of an unloaded vulcanizate of butadiene-styrene rubber (3% sulfur) at 70° C. The curves are the calculated relations: 1—According to the equation for the conventional theory of elasticity when $D = 24$ kg./cm.^{2}. 2—According to Equation (5). 3—According to Equation (6) when $D = 19.3$ kg./cm.^{2}. 4—According to Equation (2) when $G = 4.0$ kg./cm.^{2}. 5—According to Equation (5) for one-dimensional deformation.

formula conforms to the theory of elasticity and the experimental data only at low deformations (up to 50 per cent), but at larger deformations it diverges from the experimental data. Equation (5), on the other hand, agrees better with the experimental data at greater deformations (Figure 4) and deviates at small values, when $D = 19.3$, instead of 24.0 kg. per cc. according to the theory of elasticity. The inapplicability of Equations (2) and (3) at high deformations

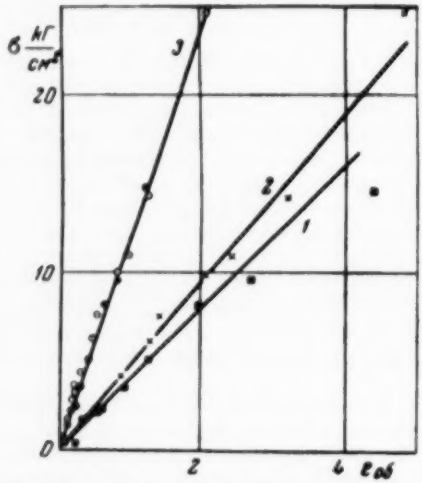

FIG. 2.—The same data as in Figure 1, drawn in generalized coordinates: 1—One-dimensional stretching according to Equation (3), $G = 4.0$ kg./cm.^{2}. 2—Two-dimensional stretching according to Equation (2), $G = 4.7$ kg./cm.^{2}. 3—Both types of stretching according to Equation (6), $E = 12.0$ kg./cm.^{2}.

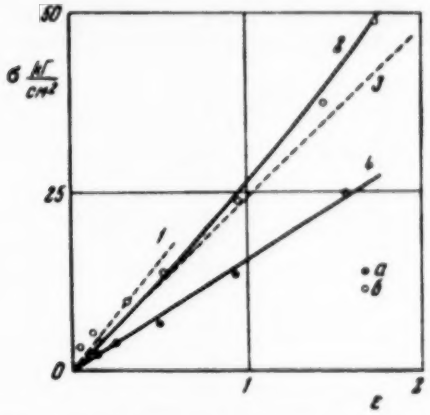

FIG. 3.—Treloar's data on (a) one-dimensional and (b) two-dimensional stretching of vulcanized natural rubber at 25° C. The curves are the calculated relations: 1—According to the formula of the theory of elasticity when $D = 30.4$ kg./cm.². 2—According to Equation (5). 3—According to Equation (6) when $D = 24.5$ kg./cm.². 4—According to Equation (5) for one-dimensional deformation.

is also seen from Figure 2, where $\epsilon_{gen.}$ is plotted along the abscissa, representing: in Equation (2): $\epsilon_{gen.} = \lambda^2 - \frac{1}{\lambda^4}$, in Equation (3): $\epsilon_{gen.} = \lambda^2 - \frac{1}{\lambda}$, in Equation (6) for one-dimensional deformation: $\epsilon_{gen.} = \lambda - 1$, and for two-dimensional deformation: $\epsilon_{gen.} = \chi \cdot \frac{\pi}{2}(\lambda - 1)$, where $\epsilon_{gen.}$ is $\epsilon_{generalized}$. In these generalized coordinates, the data for one- and two-dimensional stretching must lie on one straight line, with slope, $G = 4.0$ for the equations of Wall and Treloar and slope $E = 12.0$ for our equations. However, in the first case, the data on one-

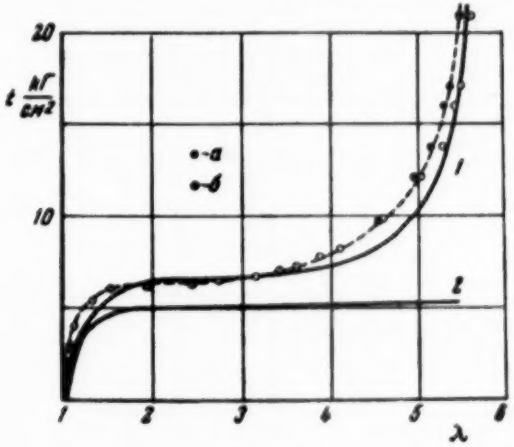

FIG. 4.—Two-dimensional stretching of vulcanized natural rubber (a) according to Treloar's data and (b) after deducting the elastic component of deformation. Curve 1—According to Equation (5). Curve 2—According to Equation (2), when $G = 5.1$ kg./cm.²

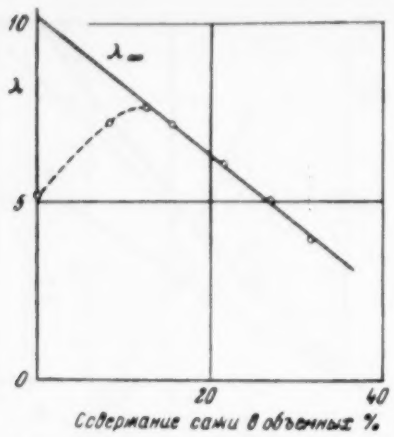

FIG. 5.—Relation of relative length (at rupture) to carbon black content of vulcanized butadiene-styrene rubber. The abscissa represents the carbon black content in percentage volume.

and two-dimensional stretching do not agree. A different value of the shear modulus is obtained for Treloar's equation (4.7 kg. per sq. cm.). This contradicts the idea that the shear modulus is a constant for the material, independent of the state of deformation.

From Treloar's data for natural rubber shown in Figure 3 (according to Treloar the shear modulus is 6.3 kg. per sq. cm.), it follows that the modulus of one-dimensional stretching $E = 15.2$ kg. per sq. cm. Hence the shear modulus[9] must be 5.1 kg. per sq. cm. and not 6.3. For this rubber under two-dimensional stretching, $\lambda_{rupture} = 5.7$ when $\sigma_{rupture} = 660$ kg. per sq. cm. Assuming that λ_∞[3] is equal to about 6, we obtain: $k \cdot T/p = 46.6$ kg. per sq. cm. and $D = 24.5$ kg. per sq. cm. Substituting these values in Equation (5), and considering that $\sigma = \lambda^2 \cdot t$, we obtain a curve which agrees well with Treloar's data (Figure

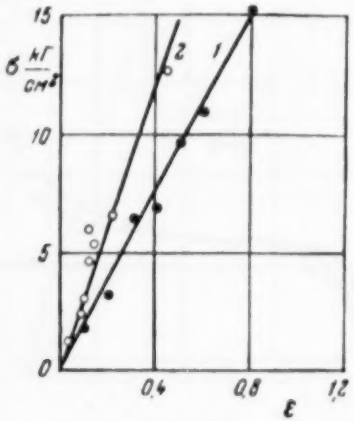

FIG. 6.—Conventional equilibrium one-dimensional (1) and two-dimensional (2) stretching of loaded vulcanized butadiene-styrene rubber at 70° C (relaxation time = 1 hour).

4). At the same time, substitution of the value $G = 5.1$ kg. per sq. cm. in Equation (2) shows considerable differences between the calculated and experimental relationships.

For practical calculations of two-dimensional deformations by stretching not exceeding 100 per cent, it is possible to use the approximate equation: $\sigma = D(\lambda - 1)$, where $D \approx \frac{\pi}{2} \cdot E$, since χ is near unity for most rubbers. In order to verify the validity of this relation for commercial rubbers, we measured one- and two-dimensional deformations of a loaded (30 parts of carbon black by weight) butadiene-styrene rubber vulcanizate. Figure 6 gives the results, which show that the relation between the moduli $D = 29.2$ and $E = 18.6$ kg. per sq. cm. is 1.57.

Membranes, valves, inner tubes, and other products undergo small two-dimensional deformations by stretching. However, certain rubber products, such as pilot balloons operate under strains up to the breaking point. Two-dimensional stretching to the breaking point takes place during the testing of latex films. In these cases, the more complex Equation (5) is applicable in describing such deformations.

CONCLUSIONS

1. With the orientation theory of deformation of the spatial network of a polymer as a basis, the equilibrium two-dimensional deformation of vulcanized rubber was calculated. Below a certain conventional limit of stretching (about 100 per cent), the deformation equation obtained gives an approximately linear relation between the true stress and the deformation.

(2) Comparison of the formulas obtained and those of Wall and Treloar with the experimental data showed that (a) the Wall-Treloar theory is inapplicable at high deformations (above 10–20 per cent), and at low deformations it conforms to the equations of the usual theory of elasticity; (b) the relations derived in this work describe medium and high deformations of rubber up to the breaking point, but deviate from the experimental data and with the theory of elasticity at low deformations; however, this discrepancy is almost negligible for vulcanized rubbers.

3. It is shown that, at small two-dimensional deformations (less than 10 per cent), it is necessary to use the equations of the conventional theory of elasticity for medium deformations, the equation of proportionality when $\sigma = D \cdot \epsilon$, where $D \approx \frac{\pi}{2} \cdot E$ (according to the theory of elasticity $D = 2E$), and Equation (5) at high deformations (above 100 per cent).

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[2] This instance of two-dimensional extension stretching is often met in practice.
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[6] The smaller is the chain in comparison with the original rubber molecule, the more accurate is this relation.
[7] The inverse Langevin function and its derivative can be represented by the following series:
$$L_*(y) = 3y + 1.8y^3 + 1.7y^5 + \cdots; \quad L'_*(y) = 3 + 5.4y^2 + 8.5y^4 + \cdots$$
[8] Treloar, *Trans. Faraday Soc.* **39**, 241 (1943); Rubber Chem. & Technol. **17**, 813, 957 (1944).
[9] This value was obtained from experiments on two-dimensional deformation.

STRESS RELAXATION OF PEROXIDE AND SULFUR VULCANIZATES OF NATURAL RUBBER *

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INTRODUCTION

Direct chemical investigation of the degradation of polymeric networks is usually impracticable owing to the experimental difficulty of insolubility and to the fact that reaction at only a small proportion of network units is sufficient to cause marked alteration of network structure. Resort has, therefore, to be made to the measurement of physical changes brought about by the chemical reactions. Change of tension at constant extension is a useful measure for this purpose, since statistical elasticity theory predicts a direct proportionality between the tension and the number of chains supporting the stress[1].

The present purpose is: (1) to describe a stress relaxometer possessing certain advantages over previous models; (2) to report on the stress relaxation of peroxide-crosslinked rubber, which can be considered from a chemical viewpoint to be the simplest possible rubber network[2]; (3) to point out some complications in the relaxation behavior of sulfur vulcanizates, and (4) to interpret the shapes of stress relaxation curves.

THE RELAXOMETER

The tension in a rubber strip kept at constant extension is measured by a helical spring in series with the strip. The length of the spring is adjusted until the opposing forces in strip and spring are balanced. This principle lends itself to a compact design of relaxometer suitable for enclosing in high-vacuum glass apparatus of a size convenient for immersing in a liquid thermostat (in preference to enclosing it in an air oven). Figure 1 is a photograph of the relaxometer and jacket.

A rubber strip A is held at constant extension along the lower part of the bar CD. The upper clamp M carries a swivel for engaging the lower end of the helical spring B. The upper end of the spring is fixed to the tapped block E, the position of which on CD is adjusted externally by rotation of the screw-thread by tungsten points of the glass key F. The tension in the spring is taken to be equal to that in the rubber when rotation of F just lifts the upper clamp off the fixed pin G. This also prevents spring recoil should the strip break. The length of the spring is measured by a cathetometer. The spring accurately obeys Hooke's law over the range of extension used, so calibration is unnecessary when expressing results in terms of reduced stress, f/f_0.

The apparatus is located centrally in the glass tube H by three phosphor-bronze leaf springs, which also act as heat-conducting paths to the relaxometer. A screw and lock-nut on the bottom of CD prevent vertical movement of the relaxometer in the tube. The assembly is immersed in thermostated paraffin

* Reprinted from the *Journal of Polymer Science*, Vol. 18, pages 201–13 (1955).

oil beyond the bottom of the glass sockets. Silicone grease keeps these vacuum-tight. The glass key is lubricated by lithium-stearate grease[3], and the occasional leakage after many turns of the key is obviated by the mercury sealing trough.

EXPERIMENTAL MATERIALS

Peroxide vulcanizates.—Deproteinized crepe was precipitated from solution to give middle fractions of molecular weight above 5×10^5 and with oxygen and nitrogen contents less than 0.2 and 0.02 per cent, respectively[4]. Di-*tert*-butyl peroxide was extracted with 40 per cent aqueous NaOH, washed, dried,

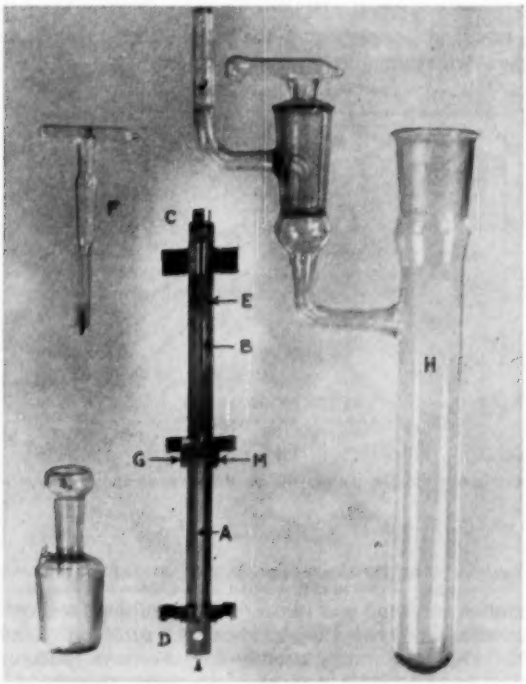

FIG. 1.—Stress relaxometer and reaction vessel.

and distilled; the fraction of b.p. 109.0–110.0° at 758 mm. Hg was collected for use, giving n_D^{16} 1.3915, C 66.0%, H 12.4%, compared with reported n_D^{16} 1.3905[5] and theoretical C 65.7%, H 12.4%.

The purified rubber was dissolved in benzene to a 1 per cent solution and cast as a film 0.1 mm. thick on Fluon (polytetrafluoroethylene) by 2–3 hours of evaporation at 60° C, in a stream of nitrogen. The film and backing were then sealed with 2 per cent peroxide in an evacuated tube and heated for 6 hours at 140° C. Strips from the cross-linked film were extracted with hot acetone for 16 hours in an atmosphere of nitrogen, dried, and stored *in vacuo*.

Sulfur vulcanizates.—Sheets of sulfur vulcanizates were made by conventional technological means. The rubber and ingredients were compounded on a 12-inch mill and then cured at 140° C under pressure in molds 0.1 mm. deep.

The thickness over the sheet was within the reproducibility of 0.01 mm. of a dial-gage thickness instrument, and over the smaller area of a single strip was probably within 5 per cent constancy (shown by the sensitive test of uniform width on stretching). Strips 5 mm. wide were cut with parallel knife edges. The two vulcanization recipes were: (1) pale crepe 100, zinc oxide 3, stearic acid 0.5, mercaptobenzothiazole 1, sulfur 3, and (2) smoked sheet 100, zinc oxide 5, stearic acid 1, Santocure 0.7, sulfur 2.5. They required, respectively, 40 and 20 minutes at 140° C for optimum cure.

Hydroquinone, pyrogallol, trinitrobenzene, and phenyl-2-naphthylamine were freshly recrystallized to the correct m.p.'s. α,α'-Diphenylpicrylhydrazyl was prepared by the method of Goldschmidt and Renn[5]. Nitric oxide was prepared in a modified Lunge nitrometer and distilled through an acetone-CO_2 trap to an evacuated storage bulb.

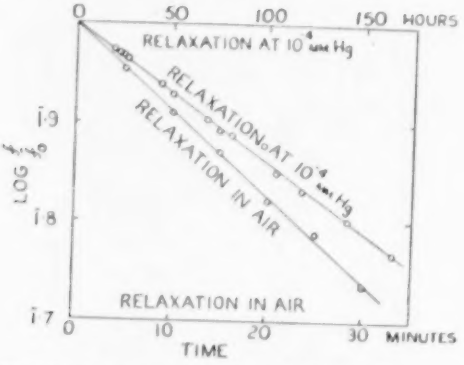

FIG. 2.—Stress relaxation of a peroxide vulcanizate in air and *in vacuo* at 120° C.

RESULTS

PEROXIDE-CROSS-LINKED RUBBERS

Stress relaxation in vacuo *and in air.*—These rubbers relaxed *in vacuo* at a rate negligible compared with that in air at the same temperature. For example, at 120° C the stress was reduced by 38 per cent in 150 hours at 10^{-4} mm. Hg pressure, and in 24 minutes in air at atmospheric pressure. The logarithm of stress varied directly with time during relaxation at 10^{-4} mm. Hg, giving a slope of about 1/400th of that observed on relaxation in air (Figure 2). Oxygen is, therefore, necessary for relaxation as normally studied. Oxygen in this case does not act merely as a radical acceptor[6], since other typical acceptors, e.g., nitric oxide and α,α'diphenylpicrylhydrazyl, do not alter the relatively very slow rate of relaxation *in vacuo*.

In oxygen at pressures from 10^{-3} to 600 mm. Hg and at temperatures from 80 to 120° C, stress changed according to Equation (1) (Figure 2):

$$f/f_0 = \exp\{-kt\} \tag{1}$$

where f is the stress at time t. No evidence of an initial nonexponential decay was detected.

A detailed quantitative investigation of dependence of rate on oxygen pres-

sure requires standardization of all the other factors influencing the rate. Unfortunately this was not succesfully achieved, despite rigorous control over all stages of preparation and purification of the cross-linked material. Rates of relaxation of different strips at 80° C were reproducible to 20 per cent, but varied at 100° C by more than threefold in extreme cases. For this reason, only trends in oxygen-pressure dependence could be ascertained. This irreproducibility was minimized by varying oxygen pressure in steps during the relaxation of a single strip.

At 80° C, successive decrements in pressure from 600 to 2 mm. caused no change of rate of relaxation, but evacuation to 10^{-4} mm. Hg reduced the relaxation to the relatively low rate previously observed at this pressure. Reintroduction of oxygen in stages caused resumption of stress decay at the constant rate (Figure 3). Oxygen concentration is, therefore, not a rate-determining

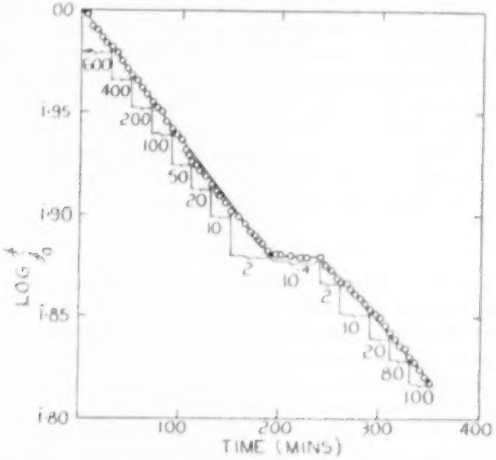

FIG. 3.—Independence of the stress relaxation rate of a peroxide vulcanizate on oxygen pressure. Figures refer to oxygen pressure in mm. Hg over periods indicated. Temperature, 80° C.

factor above 2 mm. Hg at 80° C. At 100° C, relaxation measurements on a single strip over a range of pressures was invariably prevented by sudden breakage of the strip at pressure above about 100 mm. Hg. Decay constants k of Equation (1) on a single strip up to 100 mm. Hg, however, consistently showed a pressure dependence, e.g.:

mm. O_2	10^{-4}	10^{-2}	5×10^{-2}	0.1	0.2	0.5
$k \times 10^4$ sec.$^{-1}$	3.726	4.123	4.33	5.604	9.85	11.57
mm. O_2		1	2	5	10	100
$k \times 10^4$ sec.$^{-1}$		30.71	31.51	39.73	76.18	168.3

The differences in pressure dependence indicate a change in importance of different factors affecting the mechanism of stress decay. This conclusion is supported by measuring rates of relaxation on the same strip at different temperatures; log k is not proportional to $1/T$, as shown by the following values at 100 mm. Hg:

$1/T \times 10^3$	2.916	2.874	2.832	2.794	2.755	2.717
log ($k \times 10^4$)	0.9855	1.2732	1.6051	1.8258	2.0282	2.1970

TABLE I

RATE OF STRESS RELAXATION AT 80° C IN THE PRESENCE OF OLEFIN-OXIDATION RETARDERS

Oxygen pressure (mm. Hg)	Rate constants $k \times 10^4$ sec.$^{-1}$			
	No inhibitor added	Pyrogallol 1.7%	Hydroquinone 0.5%	Trinitrobenzene 1.4%
1	—	—	4.3	5.9
2	8.6	—	5.0	6.1
5	7.6	3.3	5.1	6.1
10	8.6	2.4	5.1	5.6
20	6.3	2.3	5.4	5.8
50	7.7	2.5	5.1	5.2
100	8.1	2.4	5.0	5.6
200	—	—	5.2	6.1
500	—	—	—	6.2

An apparent activation energy of 16.7 kcal. is obtained from the results at 80 and 90° C, and of 10.7 kcal. for the results at 90° and 100° C.

Effect of olefin-oxidation retarders.—A reduction of rate was effected by adding retarders of olefin oxidation (Table I). However, the reductions of rate by phenolic retarders are much less than would have been anticipated by assuming a correspondence with their efficiencies in retarding olefin oxidation at these concentrations[7]. There are no comparative figures of the effect on olefin oxidation of phenyl-2-naphthylamine, which at 3 per cent concentration reduced the rate of relaxation to about one quarter of its original value.

SULFUR VULCANIZATES

Relaxation in vacuo.—The two typical sulfur recipes gave vulcanizates which relaxed in a vacuum of 10^{-4} mm. Hg and in purified nitrogen (Figure 4). Relaxation under these nonoxidative conditions was reproducible, and was not negligible in rate or extent compared with relaxation of similar strips in air.

Degradation in air.—Contrary to previous reports[8], decay of stress, f, departed markedly from the simple exponential Equation (1). The logarithm of stress became linear with time only after stress had decayed by more than 50 per cent in the case of the MBT-rubber (Figure 5), giving then decay constants k, at different temperatures:

Temp., ° C	115	120	125	130	135	140
$k \times 10^4$ sec.$^{-1}$	0.466	0.717	1.36	2.05	4.01	5.70

These decay constants yield an Arrhenius activation energy of 32 kcal./mole.

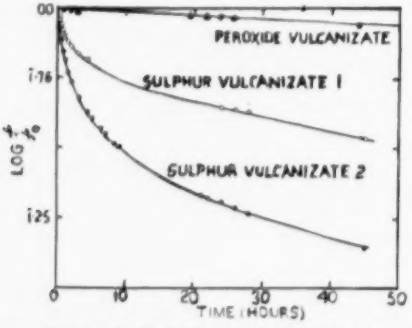

FIG. 4.—Stress relaxation of sulfur vulcanizates at 10^{-4} mm. Hg.

THEORETICAL

Before the results of the stress relaxation measurements described can be interpreted, it is necessary to consider the different forms the force-time relationship can take on the assumption of different degradative mechanisms. The agreement of the experimental results with the theoretical conclusions on the basis of a particular mode of scission enables conclusions to be drawn with regard to the mechanism responsible for the degradation. The theoretical treatment of network breakdown is presented in this section; the experimental results are considered in the light of the conclusions drawn in the subsequent discussion.

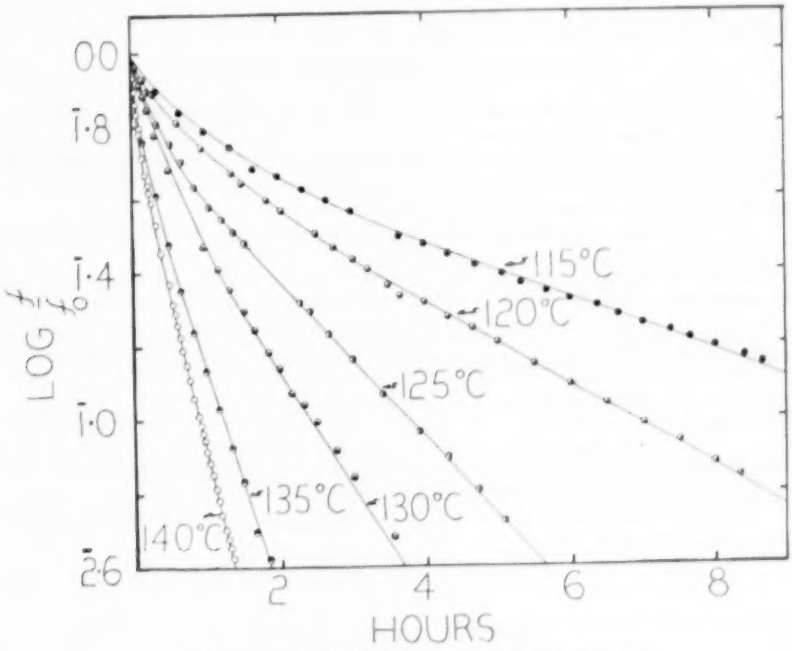

FIG. 5.—Stress relaxation in air of No. 1 sulfur vulcanizate.

The chains in a rubber vulcanizate may be classified as: (1) those not bound to the three-dimensional network (the sol fraction); (2) those bound by only one cross-link (the free-end fraction), and (3) those terminated at both ends by cross-links (the elastically effective fraction). The sol fractions in useful rubber vulcanizates are only of the order of 1–2 per cent, and do not exceed 5 per cent on relaxation of stress to the extents reported here. The fraction of chains in the sol can thus be neglected, as can also the number of cross-links, since their ratio to the number in the network is $S^2/(1 - S^2)$, where S is the sol fraction[9]. The free-end fraction can readily be accounted for since free-end chains are equal in number to twice the number of original rubber molecules[10].

The typical elastic and insolubility properties of vulcanized rubbers are imparted by the chains which are terminated at both ends by cross-links. As shown below, different modes of degradation of these effective chains provide

diagnostically different shapes of decay curves. The main two classes of scission reactions, (1) at the crosslinks and (2) at monomer units at random along the chains, are treated for reaction mechanisms likely to be encountered in practice. More complex cases, including bond formation as well as scission, can be similarly treated where warranted by availability of experimental data.

SCISSION OF CROSS-LINKS

The relation between number of cross-links in the network, X, and the number of effective chains, N, is:

$$N = 2X - E \tag{2}$$

where E is the number of chains with free ends. Directly from (2):

$$N/N_0 = (X/X_0 - E/2X_0)/(1 - E/2X_0) \tag{3}$$

Substituting in (3) the time function derived for X/X_0 from the postulated mechanism gives the predicted effective chains-time relation. The mechanisms chosen are first-order scission of cross-links and autocatalytic scission at, or determined by the position of, the cross-link (being formally analogous to chain scission accompanying olefin oxidation[11]).

(*i*) *For first-order scission of only one chemical type of cross-link*, according to $-dX/dt = kX$, substitution in (3) gives:

$$N/N_0 = (\exp\{-kt\} - E/2X_0)/(1 - E/2X_0) \tag{4}$$

(*ii*) An extension to *first-order scission of more than one type of cross-link* (later shown to be consistent with relaxation of sulfur vulcanizates) gives:

$$N/N_0 = (A_0 \exp\{-k_a t\}/X_0 + B_0 \exp\{-k_b t\}/X_0 \cdots - E/2X_0)/(1 - E/2X_0) \tag{5}$$

where A_0/X_0, $B_0/X_0 \cdots$ are the initial fractions of cross-links of types A and B, and k_a, $k_b \cdots$ are their first-order rate constants of scission.

(*iii*) *For autocatalytic scission of cross-links*, with an initial rate r_0, given by $-dX/dt = r_0 + k(X_0 - X)$:

$$N/N_0 = [(1 - r_0(\exp\{kt\} - 1)/kX_0) - E/2X_0]/(1 - E/2X_0) \tag{6}$$

RANDOM SCISSION OF CHAINS

Parts of this analysis have been carried out previously, but are included in their present context for completeness[12] or correction[13]. Changes in the number of effective chains with time for first-order and autocatalytic scission of monomer units at random along the chain are calculated, and also the relation between decrease of the number of effective chains and total number of monomer units at which scission has occurred.

If α is the probability that a monomeric unit has undergone scission in time t, the number of uncut chains of length x is:

$$N_{x,t} = N_{x,0}(1 - \alpha)^x \tag{7}$$

The distribution of lengths of effective chains in a cross-linked network is (Bueche's[12] Equation 11):

$$N_{x,0} = N_0 p(1 - p)^{x-1} \tag{8}$$

where N_0 is the total number of chains initially and p is the reciprocal of the average number of monomeric units in an effective chain. In more usual quantities, $p = m/M_e$, where m is the molecular weight of a monomeric unit and M_e is the average molecular weight between cross-links. Introducing (8) in (7) and summing for all values of x:

$$N/N_0 = p(1 - \alpha)/[p(1 - \alpha) + \alpha] \tag{9}$$

(*iv*) For *first-order scission of monomeric units* according to $-dM/dt = kM$, the number cut in time t is $M_0(1 - \exp\{-kt\})$, and hence $\alpha = (1 - \exp\{-kt\})$. Inserting in (9):

$$N/N_0 = p/(p + \exp\{kt\} - 1) \tag{10}$$

(*v*) For *autocatalytic scission of monomer units* following the rate equation, $-dM/dt = r_0 + k(M_0 - M)$, and hence with $\alpha = r_0(\exp\{kt\} - 1)/kM_0$, insertion in (9) gives:

$$N/N_0 = p[1 - r_0(\exp\{kt\} - 1)/kM_0]/ [p + (1 - p)\, r_0(\exp\{kt\} - 1)/kM_0] \tag{11}$$

TOTAL NUMBER OF CUTS

Of practical interest is the relation between total number of monomeric units at which scission has occurred (total number of cuts) to the number of effective chains cut at least once (effective cuts), since the former is the measure of degradation given by chemical means and the latter is related to the corresponding change in physical properties. For example, the number of total cuts calculated from stress decay may profitably be compared with the amount of oxygen absorbed[13]. A previous derivation[13] can be shown to be applicable only to the hypothetical case of a network of chains of uniform length.

The probability, α, is equal to the fraction of monomeric units cut in time t. Then, defining q as the moles of monomeric units cut per base mole, $\alpha = q$. Substitution in (9) and rearranging gives:

$$q = \alpha = p(N_0 - N)/p\,(N_0 - N) + N \tag{12}$$

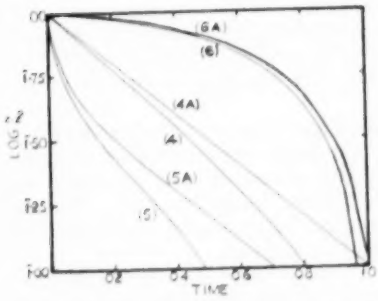

Fig. 6.—Decrease of elastically effective chains by different modes of cross-link scission, according to Equations (4), (5), and (6) and these equations neglecting the end correction (4A), (5A), and (6A).

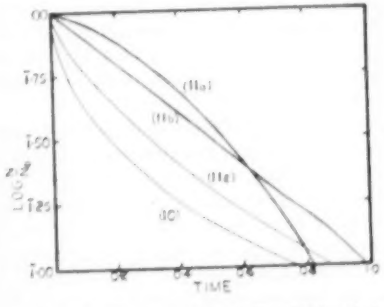

Fig. 7.—Decrease of elastically effective chains by different modes of random chain scission, according to Equations (10) and (11). Curves 11a, 11b, and 11c illustrate variations in form caused by variations in initial rate.

DEGRADATION–TIME CURVES

Figures 6 and 7 illustrate the shapes of the curves for log N/N_0 *versus* time expected from Equations (4), (5), (6), (10), and (11) for the different mechanisms of degradation. (This corresponds to the method of expressing the stress relaxation results.) Also included are curves for cross-link scission on neglecting the end corrections in these equations (since end corrections are still only a theoretical correction and their application to a degrading network is uncertain). The conclusion of practical value, stated previously[12], is amplified, namely, that different degradative mechanisms give decay curves of distinctly different patterns. In particular, first-order scission of cross-links of one type gives a linear decrease of log N/N_0 with time over a considerable extent of reaction, and first-order scission of more than one type of cross-link gives curvature followed by a linear portion.

DISCUSSION

Basic assumptions.—Two basic assumptions are made in the interpretation of the experimental work in this paper and elsewhere: (1) the validity of the statistical-theory derivation of a proportionality between the force at constant extension, f, and the number of effective chains and (2) that the stress in a rubber vulcanizate at constant extension depends only on the number of the original effective chains which remain after degradation. Both these assumptions are known to be only approximately valid. Assumption (1) is applicable to swollen rubbers, but only as a first approximation for dry rubbers[14]. However, there may be a considerable compensation for this approximation for the same sample of dry rubber at different degrees of degradation. It is also unlikely that assumption (2) holds for sulfur vulcanizates, since development of permanent set is evidence that effective chains are being produced concurrently with chain scission[15]. However, despite the inadequacies of the assumptions, the consistency of interpretations suggests that they are still useful for a qualitative interpretation of relaxation results.

Evidence for cross-link scission.—Throughout the extensive studies of stress relaxation of vulcanizates under oxidizing conditions, by Tobolsky[16] and others, the decrease of stress is approximately exponential with time. This exponential decay is also obtained for the relaxation *in vacuo* of polysulfide rubbers[17]. Along with the present work, there appear to be no examples of random chain scission, judged by the shape of relaxation curves. The close agreement of the relaxation of peroxide vulcanizates with the empirical exponential law is a clear-cut example of the simplest type of cross-link scission (Figure 6, curve 4A). The sulfur vulcanizates relax in accordance with the scission of two types of cross-links.

The great differences in rates of relaxation and response to variation of temperature and oxygen pressure of peroxide and sulfur vulcanizates are inconsistent with chain rupture, since the small amounts of cross-linking material would not be expected to modify so drastically a random scission process. Previous workers have shown that wide variation in polymer chain with a common type of cross-link produces only minor variation in behavior[8].

The relaxation, which depends on the presence of oxygen, would be likely to be associated with autocatalytic oxidation if random chain scission were operative, and give curves of the type (11A), (11B), or (11C) of Figure 7. The small effect of oxidation retarders is also inconsistent with scission associated with the propagation steps of olefinic oxidation[7].

TABLE II

FRACTIONS OF CROSS-LINKS OF TWO TYPES AND THEIR RATES OF SCISSION EVALUATED FROM THE RELAXATION DATA

Temp. (° C)	A_0/X_0	B_0/X_0	k_a, $\times 10^5$ sec.$^{-1}$	k_b, $\times 10^5$ sec.$^{-1}$
140	0.365	0.635	4.25	5.70
135	0.411	0.589	2.54	4.01
130	0.397	0.603	0.793	2.05
125	0.369	0.631	1.01	1.36
125	0.415	0.585	0.384	0.717
115	0.411	0.589	0.334	0.466

Peroxide vulcanizates.—Oxygen is required for stress relaxation, since relaxation *in vacuo* is negligibly slow, and can be initiated and arrested by the rapid addition and removal of oxygen, respectively. However, over a wide range, the rate is independent of oxygen concentration at 80° C, and so oxygen does not participate directly in the rate-determining step. Oxidation cannot be appreciably prior to scission, otherwise induction and decay periods would be detectable. Also, if oxygen simply prevented recombination after scission, substances such as α,α'-diphenylpicrylhydrazyl and nitric oxide *in vacuo* should be capable of acting similarly[6], and the rupture of carbon-carbon bonds at 80° C would have to be invoked. An equilibrium complex of cross-links with oxygen could explain the kinetic results, but seems improbable on chemical grounds.

The relaxation curves strongly suggest scission only at the cross-links. The chemical reactivity near the cross-link may be explicable by the unusual groupings of double bonds and tertiary carbon atoms, but it seems surprising that all cross-links rupture according to a simple first-order rate expression in view of the number of isomeric structures possible[3]. It is possible that this is only an apparent first-order decay and that more complex decay might be observable if more extended reaction could have been measured.

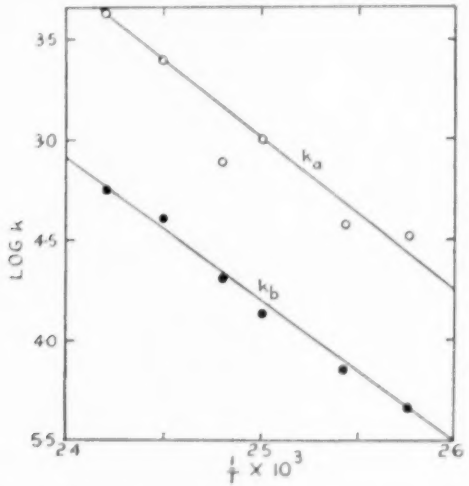

FIG. 8.—Variation of stress relaxation rate constants with temperature. No. 1 sulfur vulcanizate relaxed in air.

Sulfur vulcanizates.—The shape of the relaxation curves indicates first-order degradation of more than one type of cross-link (Figure 6, curve 5A). Qualitative comparisons are strengthened by applying Equation (5) to the data. The theoretical curves of Figure 5 were constructed with values of the parameters given in Table II. Specification of only two types of cross-link rupture is necessary, and their calculated proportions are reasonably constant. Further, the associated rate constants give satisfactory linearity on plotting for determination of activation energy (Figure 8).

The activation energy calculated from the linear part of the relaxation curves (32 kcal./mole) agrees closely with that obtained for other sulfur vulcanizates, including those of synthetic rubbers[3]. The activation energy for the more rapid process was less accurately determined, owing to lack of discrimination by the data between theoretical curves with similar values of k_a, but is within a few kcal. of the same value (35 kcal./mole for the linear plot of Figure 8). This explains the persistence of curvature of the relaxation graphs to the same extent of degradation in the temperature range studied. At the lower temperatures of normal vulcanizate aging, a reversal of the relative rates of the processes may occur, and a satisfactory extrapolation of results to this temperature would require an accurate determination of temperature coefficients.

SYNOPSIS

The stress-relaxation behavior of peroxide and sulfur vulcanized natural rubber has been investigated, using a relaxometer of new design. The peroxide vulcanizates do not degrade significantly *in vacuo*, and degrade by an exponential decrease of stress with time in oxygen. The vulcanizates from the two sulfur recipes used give stress relaxation *in vacuo* and more rapid relaxation in oxygen. A theoretical analysis provides the shape of stress-time curves anticipated for various modes of network degradation. The present data and other published results are consistent with a mechanism of scission at the cross-links and not at random along the chains. The peroxide vulcanizates are interpreted as decaying by a first-order scission of cross-links and the sulfur vulcanizates by first-order scission of two types of cross-link. The uncertainties still present in interpreting stress relaxation data are discussed.

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FILLER REINFORCEMENT AND TEAR RESISTANCE IN THE LIGHT OF THIXOTROPY *

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THIXOTROPY

A deformation is described as thixotropic[1] if the resistance to deformation decreases during the course of deformation and if the original rheologic properties return again when at rest (reversible softening under mechanical loading).

THIXOTROPY DURING SIMPLE STRETCHING OF FILLED MIXES

From this aspect, Mullins[2] considers the influence of repeated deformation of filled rubber mixes as thixotropy which occurs particularly with reinforcing fillers. Nevertheless, this type of thixotropy can be regarded as a type with a particularly long recovery time, where there is no yield point and where it is questionable where the original condition is exactly recovered. These phenomena are observed with both unvulcanized and vulcanized mixes. In the case of unvulcanized mixes with carbon black[3], Figure 1a shows how the torsional resistance in the rotation plastometer decreases as the shearing time increases; Figure 1b shows that the resistance increases again on storing at 100° C. It is seen here that this effect is scarcely present with the unfilled mix, but becomes very evident with the reinforcing fillers. Figure 2 gives a typical picture of vulcanized mixes[4], from which it may be seen that the decrease and increase of the modulus on movement or rest is linked with a decrease or increase of the electrical conductivity.

EXPLANATION OF THIXOTROPY IN SIMPLE STRETCHING

Every alteration of the mechanical properties of a filled rubber mix may be described theoretically as the consequence of an alteration in the state of the linkages. The linkages in question can be divided into three groups:

(a) Rubber-rubber.
(b) Rubber-filler.
(c) Filler-filler.

The modulus of a filled mix is the stress necessary to achieve a definite elongation, and it may be regarded as the resultant of the effect of the above-mentioned three groups of linkage energies. In the discussion of (b), the deciding question nowadays is whether only chemical linkages between filler and rubber are present[5] or whether there are principally easily destroyed secondary linkages and perhaps, in addition, individual chemical linkages[6]. Mullins again

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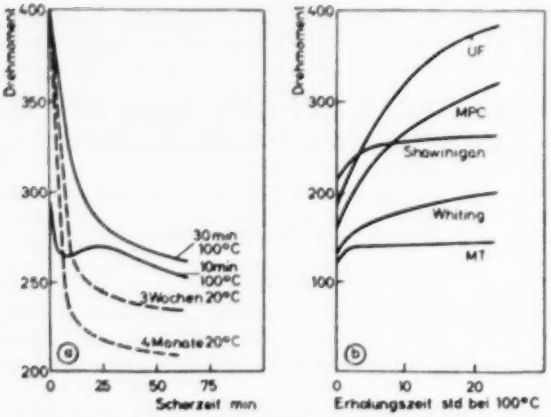


FIGS. 1a and 1b.—Thixotropy in unvulcanized rubber mixes. a) During flow in the rotation plastometer, the viscosity gradually decreases. b) At rest, the viscosity returns to its original value. On the graphs, Drehmoment = torsional moment; Wochen = weeks; Monate = months; Scherzeit = shearing time; and Erholungszeit = recovery time in minutes; and Erholungszeit recovery time in hours at 100° C.

found that the modulus of these filled mixes is lowered by elongation, and he concludes from this that the lowering is connected with a destruction of linkages.

In the opinion of the present authors, a new formation as well as this destruction of linkages during deformation should be the explanation of this lowering of the modulus; since every alteration in the linkage-state, occurring as a consequence of a deformation, will in general facilitate a repetition of the deformation. Such newly formed linkages will certainly be without stress at the moment of the setting up, but can during the recoil take up precisely the stresses opposed to the direction of elongation. They will thus contribute a negative amount to the modulus, i.e., lower the modulus (Figure 3). Such

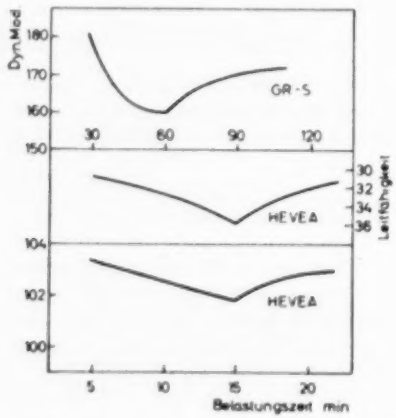


FIG. 2.—Decrease of the modulus of elasticity of vulcanized mixes during increasing dynamic loading and subsequent increase in the state of rest. The electrical conductivity runs parallel with it (mixes with about 50 parts of carbon black: 70° C). On the graph, Dyn. Mod. = dynamic modulus; Belastungszeit min. = time of stressing in minutes; and Leitfahigkeit = conductivity.

considerations show that the assessment of modulus measurements is a highly complicated matter. As a contrast with this, we have the measurement of electrical conductivity, which tells us something unequivocally in this case about the destruction of carbon black-carbon black linkages. Swelling measurements also provide clear information insofar as they form a quantitative scale for the destruction of linkages of definite strength. This scale can be matched even more finely by using various swelling agents.

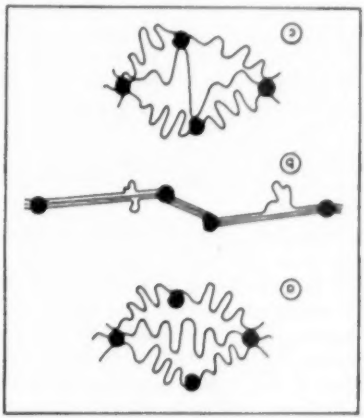


FIG. 3.—Rubber-carbon black mix.
(a) before
(b) during } elongation
(c) after

In discussing (c), the decisive questions are:

(1) Whether the filler particles cohere as frameworks and whether these frameworks can be destroyed. Some workers[7] have divided these carbon black-carbon black linkages into two groups of different strengths (breakable and unbreakable). More recent considerations[6] show, on the other hand, that presumably a continuous spectrum (that is to say, not two groups) of centers of attraction of different energy contents on the carbon black surface is present. This will make a difference in the coherence of the neighboring carbon black particles as well as to the adhesion to the rubber molecules.
(2) Whether the filler particles which are separated are present in the form of coherent clouds[8].
(3) Whether the filler particles are completely separate, so that the mechanical cohesion depends wholly on the rubber molecules.

Probably most of the rubber-carbon black bonds and carbon black-carbon black bonds are easily destroyed[9], even at very low elongations. It is not so certain whether, in this case, the few high-energy bonds are destroyed.

One important question here is whether a complete loosening of the carbon-black particles is practicable. This is certainly not the case, and even in mastication the cohesion is more or less maintained. The partial destruction is indeed largely wiped out after vulcanization; obviously at the temperature of

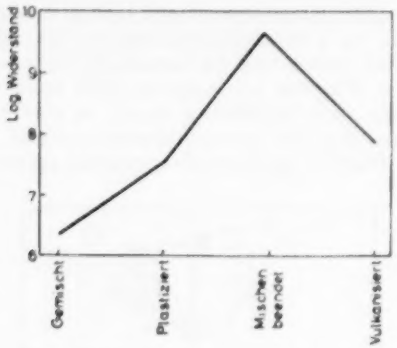


FIG. 4.—Changes of the electrical resistance of a carbon black mix during the manufacturing process. The legends indicate from left to right: log of the resistance, mixed, plasticized, end of mixing, vulcanized.

vulcanization the particles find an opportunity of taking up once more the positions most favorable from the energy point of view. In Figure 4 this behavior is represented by the alteration in electrical resistance. Dannenberg[10] observed by means of electron microscopy that the minimum size of aggregates soon adjusts itself on mixing. With mixes of a Butyl rubber base it has been shown[11] that the aggregates, for more than half, have a size of 0.1 to 1.0. The evidence shown in Figure 4, that the electrical conductivity decreases during deformation and then returns once more on storage, supports the assumption of a framework structure on the one hand and its fragility on the other hand.

DEPENDENCE OF TEAR RESISTANCE ON DIRECTION

In addition to indicating the thixotropic effect, Mullins points out the orientation which remains permanent after the stretching and releasing of filled mixes, and which he measured as anisotropy in swelling in solvents. Our experiments show that this orientation can be determined accurately by the Delft

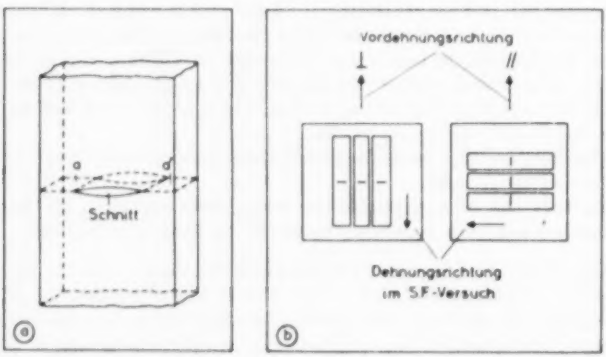
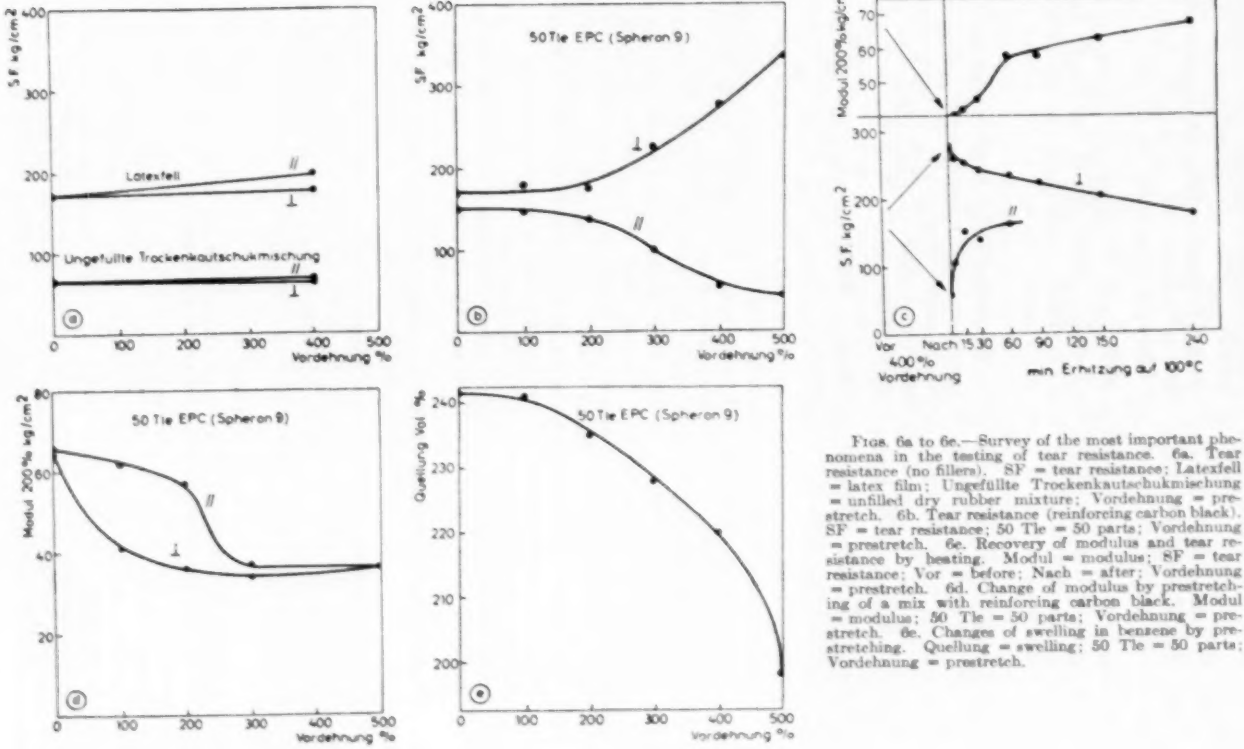


FIG. 5a.—Testing tear resistance by the Delft method. (On the diagram, Schnitt is cut.)
FIG. 5b.—Punching out the test bars in tear resistance testing in two directions by the Delft method. ⊥ the tear propagates itself transverse to the direction of prestretching; ‖ the tear propagates itself parallel to the direction of prestretching. (S.F. is tear resistance.)



FIGS. 6a to 6e.—Survey of the most important phenomena in the testing of tear resistance. 6a. Tear resistance (no fillers). SF = tear resistance; Latexfell = latex film; Ungefüllte Trockenkautschukmischung = unfilled dry rubber mixture; Vordehnung = prestretch. 6b. Tear resistance (reinforcing carbon black). SF = tear resistance; 50 Tle = 50 parts; Vordehnung = prestretch. 6c. Recovery of modulus and tear resistance by heating. Modul = modulus; SF = tear resistance; Vor = before; Nach = after; Vordehnung = prestretch. 6d. Change of modulus by prestretching of a mix with reinforcing carbon black. Modul = modulus; 50 Tle = 50 parts; Vordehnung = prestretch. 6e. Changes of swelling in benzene by prestretching. Quellung = swelling; 50 Tle = 50 parts; Vordehnung = prestretch.

tear-resistance test, which makes it possible to widen the tear in any direction desired[12].

If the vulcanized material is prestretched before punching out the specimens, choosing the direction of prestretching to be parallel with, or at right angles to, the eventual direction of tearing, the following phenomena are found[13].

(1) Prestretching has very little effect on the tear resistance of vulcanized pure-rubber mixes (latex sheet or dry rubber); it is well known that, with mixes of this kind, even the modulus is not altered by prestretching.
(2) Reinforcing fillers, in particular channel blacks, call for a very pronounced two-direction effect[14]. In the parallel direction, the tear resistance is reduced to the figure for unfilled mixes by prestretching, but in the vertical direction, on the other hand, it is greatly increased, indeed up to the figure for tensile strength (Figure 6b). These changes in the tear resistance take effect first after about 250 per cent prestretching.

The time of prestretching has no effect on these changes of tear resistance. There is no reversion at room temperature.

(3) After heating for some hours at 100° C, the vertical tear resistance once again assumes the same value as without prestretching. For this to happen with the parallel tear resistance, a few quarter hours are sufficient (Figure 6c). The same applies, as is well known, to the modulus.
(4) After prestretching of filled mixes, the modulus in both directions is reduced (Figure 6d). Prestretchings over about 300 per cent do not reduce the modulus further. The electrical conductivity is also reduced in both directions. Measurements show[15] that with stretching above 300 per cent the conductivity is not further reduced.
(5) With regard to swelling in solvents, Mullins has shown that the swelling capacity increases parallel to the direction of prestressing, but is distinctly reduced perpendicular to this direction. We have measured the total volumetric swelling, and confirm Mullins' supposition that prestressing gives a distinct reduction of the swelling capacity (Figure 6e).

EXPLANATION OF THE TWO-DIRECTIONAL EFFECT OF TEAR RESISTANCE

The most important observation is certainly that of Figure 6b, i.e., that with reinforcing fillers the tear resistance is very different after prestretching in the two principal directions. We are faced furthermore with a series of observations which obviously partly contradict each other, as is evident in Table 1.

TABLE 1

ALTERATION OF THE PROPERTIES OF CARBON BLACK MIXES IN TWO DIRECTIONS AS A RESULT OF PRESTRETCHING

	Alteration by prestretching		Range of prestretching (in %)
	⊥	∥	
Modulus	−	−	below 250–300%
Conductivity	−	−	below 250–300%
Tear resistance	+	−	above 250–300%
Swelling	−	+	above 250–300%

− decreasing.
+ increasing.

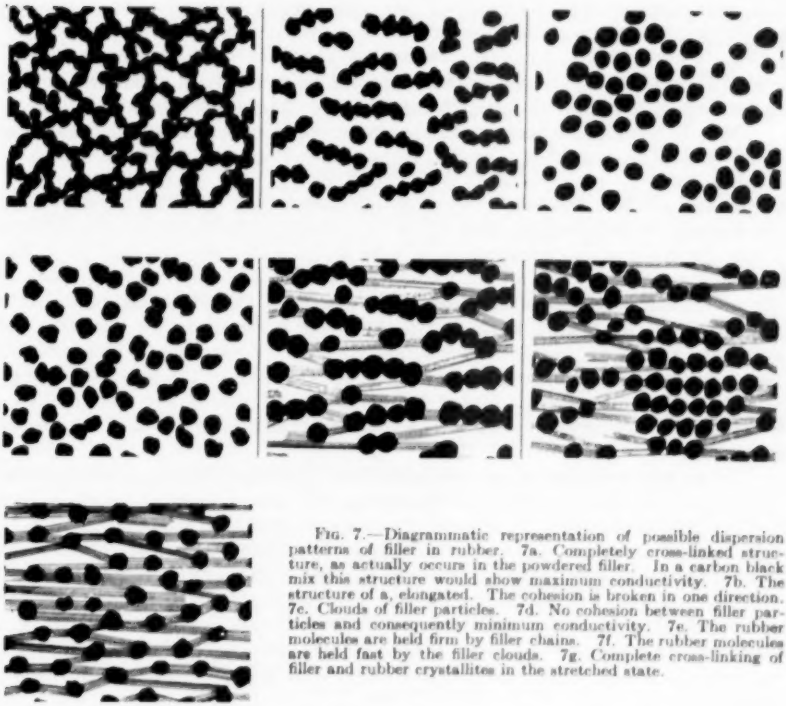


FIG. 7.—Diagrammatic representation of possible dispersion patterns of filler in rubber. 7a. Completely cross-linked structure, as actually occurs in the powdered filler. In a carbon black mix this structure would show maximum conductivity. 7b. The structure of a, elongated. The cohesion is broken in one direction. 7c. Clouds of filler particles. 7d. No cohesion between filler particles and consequently minimum conductivity. 7e. The rubber molecules are held firm by filler chains. 7f. The rubber molecules are held fast by the filler clouds. 7g. Complete cross-linking of filler and rubber crystallites in the stretched state.

The negative effect on the first two values would suggest a breaking-up of the framework. On the other hand the positive effect (in one direction) on the latter two values would suggest a reinforcement of the structure.

Let us first consider the swelling. In prestretching, linkages certainly are broken, because rubber molecules are torn away from the carbon black particles at certain places, but at the places left vacant, other rubber molecules will adhere. In this reconstruction there are no reasons for assuming the occurrence of linkages richer in energy; there will be merely a regrouping. At the same time, according to Figure 3, certain pieces of chain may form shorter linkages (mainly transverse to the direction of elongation), and this may be the explanation of the reduction of swelling in this direction.

We shall now attempt to interpret the alterations of tear resistance by prestretching. Figure 7a shows the structure of the carbon-black powder; the question is left open as to whether or not this is still present in a rubber mix to its full extent. With the stretching of a filled vulcanizate we can now imagine certain possibilities: e.g., as in Figure 7b, where chain-type portions of the structure are left intact, in Figure 7c where clouds of filler particles are left[16], and in Figure 7d, where only individual particles are left. These three possibilities can be fitted into our interpretation. The sole additional assumption which we need to make is that, on release of the stress, the rubber molecules rapidly return to the unorientated condition (the entropy effect), but that, at

the same time, the filler particles cause a restriction according to the following possibilities:

(a) The filler structures remain oriented as a result of potential energy effects between the particles themselves (Figure 7b or c).
(b) The filler particles hold the rubber molecules firm after the release of stress as a result of potential energy effects between filler and rubber.

It is as yet not possible to decide which case we do, in fact, have here. In the opinion of the authors, case 7b or 7c is most probable with carbon-black mixes, for the residual deformation of these mixes is only about 5 per cent of the elongation applied. We are, therefore, inclined to assume a slipping-back of the molecules, which is conceivable on the basis of the loosening of linkages (the Mullins effect) and which, with the assumption of a new formation of linkages (Figure 3), will lead to internal stresses. According to this idea the recovery by heating (Figure 6c) would be attributable to the potential energy thresholds being crossed at higher temperature and also to the filler particles reverting to the original condition as a result of the entropy effect of the rubber molecules.

Let us now consider the alterations of the tear resistance by prestretching. In the parallel direction the tear resistance will have decreased, because, as a result of the orientation of particles, there is a pronounced splitting effect. In the vertical direction, on the other hand, the orientation will actually act against the tearing, because the shearing stresses in the endangered portions are distributed by the carbon black particles or by the rubber-carbon black complex over a larger surface and, therefore, are weakened individually. The fact that these effects disappear again at a higher temperature (100° C) (Figure 6c) leads to the assumption, mentioned already, that this orientation is destroyed again.

The observation (Figure 6a) that this two-directional effect does not occur with unfilled mixes is then understandable without more ado. The rubber molecules are certainly orientated likewise during elongation, but the reduction of entropy thereby is the reason for them returning immediately into the unoriented state, a tendency which they can obey quantitatively, because, during the deformation of these molecules, no potential energy changes come into the picture[17].

If, on the other hand, we start from the known fact that grades of rubber (Hevea) crystallizing by elongation exhibit a much higher tear resistance than do the noncrystallizing, it is seen that crystallization plays a part here. We can picture that the tear as it progresses produces a stress concentration, which concentrates the effect of the elongation over the softer amorphous regions between the crystallites less capable of elongation. The crystallites formed during the process of elongation will locally block the tearing process, and the more crystallites there are and the better their cohesion, the higher will be the tear resistance. With Buna, etc., we have the extreme case that no crystallites at all are present, and thus the tear will extend itself with very little resistance.

The reinforcement of tear resistance effected by carbon black may now be attributed to the fact that, with elongation, structures as in Figure 7g are formed, whereby there is formed a continuous network of rubber crystallites and carbon black crystallites. The fact that the tear resistance increases in the vertical direction by prestretching, but decreases in the parallel direction may now be connected with the fact that the newly formed, and somewhat

resistant, linkages favor this orientation of crystallites by means of carbon black in the one direction and hinder it in the other. The assumption according to which crystallite orientation plays a decisive part in tear resistance is based on the observation (Table 1) that the tear resistance changes and the decrease of swelling begins at about 250–300 per cent prestretching, i.e., at about the elongation at which crystallization also becomes perceptible.

BEHAVIOR OF VARIOUS FILLERS

All the reinforcing fillers so far investigated give, more or less, an anisotropy of tear resistance after prestretching. Most of the fillers indicate a phenomenon which was not indicated in Figure 6, namely, that the tear resistance as a func-

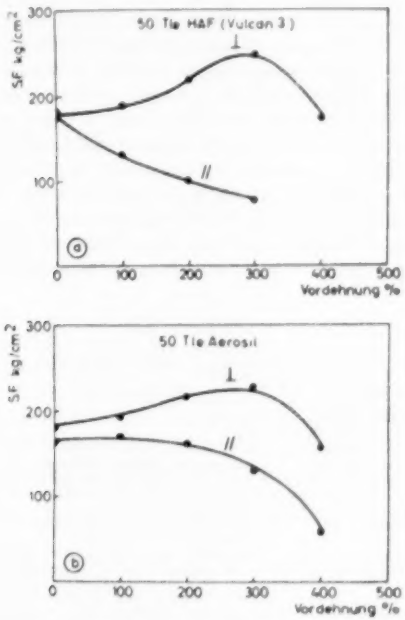


FIG. 8.—Tear resistance passes, with increasing prestretching, through a maximum. 8a. Furnace black. 8b. White filler. SF = tear resistance; 50 Tle = 50 parts; Vordehnung = prestretch.

tion of prestretching passes through a maximum, as shown in Figure 8 for a furnace black (a) and for a white reinforcing filler (b). It appears that, on passing through this maximum, the mix becomes subject to internal breaking up. It is even possible that vacuoles are formed[18], for after heating to 100° C we get greatly fluctuating values for tear resistance, which often lie a good way below the initial values.

CONCLUSIONS

Although the changes which filled rubber mixes exhibit on elongation represent a definite softening, we nevertheless believe that, with the collected facts we have shown, that this behavior involves a constructional element, inasmuch as a permanent resistance is built up against repeated deformation in the same

direction. A rubber object certainly loses a part of its rigidity in service (and this should be taken into account in manufacture), but it is also reinforced in a definite manner by the stressing.

SUMMARY

Rubber mixes containing reinforcing fillers may be regarded as being thixotropic, with a very long recovery time. The explanation of this is found in the destruction and the reconstruction of filler-rubber linkages and filler-filler linkages, which adhere to each other as a result of a continuous spectrum of energies of attraction. It is assumed that the rubber-filler complex becomes oriented during the stretching of filled mixes. With unfilled mixes, the rubber molecules are able to spring back again, when the stress is released, into the position which is mostly favorable from the point of view of entropy. As a consequence of the introduction of potential energies by the incorporation of reinforcing fillers, the rubber molecules have their mobility adversely affected, as a result of which a definite orientation may be maintained when the stress is released. For instance, after prestretching of these mixes, a significant increase of the resistance to continued tearing at right angles to the direction of elongation and a decrease parallel to this direction are found. This partial increase of the tear resistance, which is not encountered with unfilled mixes, will presumably contribute, as does crystallization, to reinforcement. This increase indicates that the tearing forces in a stretched mix are distributed in one direction over a large surface area. A series of associated phenomena are explained.

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[11] Ford and Mottlau, *Rubber Age* (N. Y.) **70**, 457 (1952). In Butyl rubber, in which the aggregates are larger, the dispersion seems to be poorer than in natural rubber.
[12] In the Delft tear resistance method (Fig. 5), the specimen is stretched at a velocity of 300 mm./min., and the indicated breaking force divided by the cross-section $a + a'$, so that the final value (in kg./sq. cm.) is comparable to the tensile strength. It is clear that the tear resistance can never be greater than the tensile strength. In the case where no stress concentration occurs, the tear resistance must be equal to the tensile strength. With carbon black-filled rubber, this actually occurs after 500 per cent prestretching (see Fig. 6b).
[13] The vulcanizates were prepared with 1 part Vulkacit-CZ and 2 parts sulfur, with the exception of the Aerosil mix, which contained 3 parts Vulkacit-CZ and 3 parts sulfur. Vulcanization was for 20 min. at 142° C.
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EFFECT OF THE TEMPERATURE OF POLYMERIZATION ON THE STRUCTURE OF BUTADIENE-STYRENE COPOLYMERS *

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The addition of monomer molecules to the growing polymer chain during the polymerization of dienes may take place in several ways. In the polymerization of butadiene, the addition takes place in the 1,2– and 1,4-positions. In the latter case polymer chains are obtained with structural variations, e.g., the position of CH_2 groups at the double bonds is *cis* or *trans*. The resulting polymer chains vary in configuration. It is of interest to determine how the configuration is affected by different conditions of polymerization. Several papers related to the subject are to be found in the literature[1].

In this work, we studied with an infrared spectrometer the compositions of butadiene-styrene copolymers prepared at different temperatures. Also determined was the content of the various configurations of butadiene links in the polymer chains.

The samples were prepared by polymerizing emulsions by the dilatometric method in the absence of oxygen. A satisfactory emulsion was obtained with a magnetic stirrer inserted into the dilatometer (Figure 1). The rotation of the stirrer (activated by a magnet attached to the axis of a motor under the thermostat) sucked the upper part of the liquid through the upper opening (1) and expelled it through the side opening (2); this assured emulsification.

The polymerization was conducted between −15° and −38° C. Glycerol was used as an antifreeze at temperatures below 0° C. For comparison, experiments were conducted in the presence of glycerol also at temperatures above 0° C.

The kinetic data are given in Figure 2. The yield of the polymer is expressed in grams per liter of the aqueous phase. By aqueous phase is meant the aqueous solution of the emulsifier (a mixture of sodium salts of sulfacids of the saturated fatty acid series with 12–18 carbon atoms) and of the initiator (isopropylbenzene hydroperoxide and potassium ferrocyanide).

The kinetic data show that the yield increases with increasing temperature of polymerization both in the presence of glycerol and in its absence; at equal temperatures the yield is greater in the tests without glycerol than in those with it.

The activation energy of the polymerization was determined from the relation of the reaction rate to temperature. In both cases the activation energy equals about 9 kcal./mole. The rapid decrease of the rate of polymerization at 38° C (unlike at other temperatures) is probably related to the greater speed of decomposition of the initiator at this temperature.

The infrared absorption spectra of the polymers obtained were measured with the monoray Hilger recording spectrometer using a sodium chloride prism.

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FIG. 1.

The spectra were determined in carbon disulfide solution. The samples were prepared in the following manner. The latex produced was coagulated with methanol and a sodium chloride solution. The separated polymer was washed with hot water to remove the emulsifier and was reprecipitated several times with methanol from a carbon disulfide solution. The precipitation of the polymers was conducted in a stream of nitrogen. The precipitated polymer was

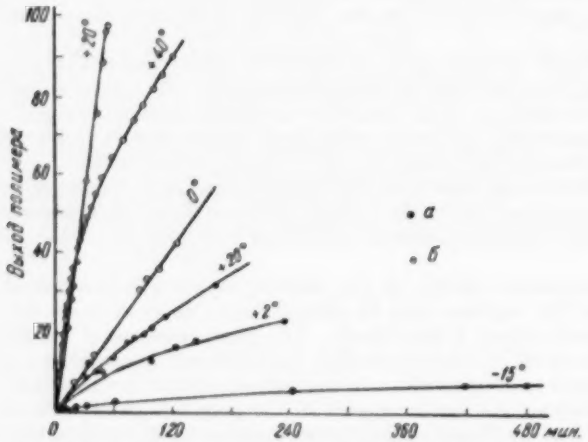

FIG. 2.—Kinetics of butadiene-styrene copolymerization at various temperatures. *a* = experiments with glycerol ●; *b* = experiments without glycerol ○; Abscissa = minutes; Ordinate = yield of polymer.

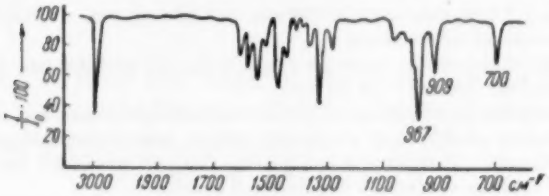

FIG. 3.—Spectrum of the butadiene-styrene copolymer.

dissolved in carbon disulfide, and the solution was kept under vacuum to remove the residual methanol.

The concentration of the polymer in solution varied between 16.6 and 40.9 g./l., and was determined by weighing the residual dry solids after the carbon disulfide was evaporated from a known amount of polymer solution. The thickness of the layer used for measuring the spectra was 0.2 mm.

The spectrum of the butadiene-styrene copolymer is shown in Figure 3. The number of styrene bonds in the polymer was determined by the differential intensity of the band in the 700 cm.$^{-1}$ region (characteristic of the benzene ring). The composition of the various configurations of butadiene links was determined by measuring the differential intensity of the 967 and 909 cm.$^{-1}$ infrared bands which correspond to the *trans*- and the 1,2-configurations. These bands are related to the deforming fluctuation of the —C=C—H bonds. The Lambert-Beer law was used to calculate the relative quantities of styrene links, 1,2- and *trans*-configurations in the polymer. The content of *cis*-configurations of the butadiene links was calculated by difference.

The specific coefficient of extinction K_{700} for the band in the region 700 cm.$^{-1}$ was determined from the intensity of this band in the spectrum of polystyrene which had been prepared by emulsion polymerization; $K_{700} = 1.7$ liters/g. cm.

For the determination of the contents of the *trans*- and 1,2-configurations we used the specific extinction coefficients reported in the literature[2]. It should be noted that the results reported by the various authors vary considerably; however, the relation of the specific extinction coefficients for the investigated absorption bands were approximately the same. Using our extinction coefficient for the styrene links and the correlations taken from the literature, we calculated the following specific extinction coefficients: for bands in the 967

TABLE 1

Experimental temp. (° C)	Composition in percentage			
	Of styrene bonds	Of butadiene bonds		
		1,4 *trans*	1,2	1,4 *cis*
Experiments without glycerol				
0	16	56	13	15
+20	16	47	11	26
+38	15	39	12	34
Experiments with glycerol				
−15	32	53	12	3
0	(42)	51	10	—
+20	32	54	12	2

cm.$^{-1}$ region, 1.7 l./g. cm.; and for 909 cm.$^{-1}$, 2.18 l./g. cm. These figures were used in subsequent calculations.

The width of the slot for measurements in the 967 and 909 cm.$^{-1}$ regions was 0.18 mm., and for 700 cm.$^{-1}$, 0.40 mm.

The calculation of quantities of the various configurations was made, counting the backdrop of diffusion which was added, not to the absorption, but to the transmittance. Precision of the results obtained was ±2.5 per cent on the average. The data obtained are given in Table 1.

The data in Table 1 show that for polymers produced without glycerol, increasing the polymerization temperature from 0° to 38° lowers the quantity of the *trans*-isomer by 17 per cent. Changing the polymerization temperature within this range, using glycerol, does not affect the composition of the polymer; however, in this case, the polymers contain twice as much styrene. To check this phenomenon, we determined the unsaturation of the polymers investigated by the Vasiliev method[3] (the action of bromine iodide on a carbon tetrachloride solution of the polymer). The data thus obtained are given in Table 2. The

TABLE 2

Experimental temp. (° C)	Presence of glycerol	Unsaturation calculated for 1 g. of polymer (%)	Unsaturation calculated from the amount of butadiene (%)
+38	−	79	93
0	−	76	91
+20	+	63	93
0	+	62	92

results show that the unsaturation (on the basis of 1 g. of the polymer) is considerably less in polymers prepared in the presence of glycerol than in those prepared without glycerol.

The unsaturation, calculated only for the butadiene links (considering the amount of styrene in the polymer) is identical in both cases, which corroborates the results for styrene obtained by the spectroscopic method.

The relatively small variations of the amount of the various configurations obtained at different temperatures show that the effect of polymerization temperature on the properties of the polymer[4] can hardly be related only to the relationship between the *cis*- and *trans*-configurations, as has been proposed by some authors[2].

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SOME FEATURES OF THE KINETICS OF CATALYTIC COPOLYMERIZATION. COPOLYMERIZATION IN THE BUTADIENE-ISOPRENE AND BUTADIENE-STYRENE SYSTEMS *

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In the course of research into carbon-chain polymerization under the influence of the acid-type catalysts, aluminum chloride, boron fluoride, stannic chloride, and others, a series of investigations have established the fundamental mechanisms of these chain processes, indicating that they have an ionic character[1]. On the basis of this research, it was suggested that the active center in carbon-chain polymerization is a compound with a tervalent positive carbon atom at the end.

The kinetics of catalytic copolymerization had not been studied until the present. There has been only a little work published in connection with determining the composition of copolymers and calculating the copolymerization constants for the systems in question.

We initiated some research into the dependence of the speed of catalytic copolymerization on the composition of the original mixture, in conjunction with a determination of the speeds of separate polymerization of the monomers involved, since a comparison of data on the kinetics of copolymerization with that of separate polymerization gives a more complete representation of the mechanism of the process. A study was made of the speed of copolymerization of the systems: isoprene-butadiene and styrene-butadiene, and also of the kinetics of separate polymerization of these monomers. Polymerization was carried out in ethyl chloride with stannic chloride as the catalyst, at 0° C, by the dilatometric method.

During the investigation of the separate carbon-chain polymerization of isoprene and of styrene, we observed an increase of the speed of the reaction with time, such as did not take place during the radical polymerization of these compounds. With styrene, this phenomenon was observed at temperatures of 20° C and above in high concentrations of styrene (about 2.5 moles/l. or more)[2]. With isoprene an increase of speed with time took place also at low concentrations of isoprene (about 0.5 mole/l. or more) at 0° C. The increase of the polymerization speed of isoprene and styrene with time was not observed at low temperatures (−80° C) nor in the presence of added hydrogen chloride[3]. It was established that this occurrence depends on an increase of the speed of initiation. In the course of the investigation of the copolymerization speed of butadiene with isoprene and with styrene, we also noted certain features of the kinetics of the process which are not found in the radical polymerization of these systems.

According to our data, in an ethyl chloride solution, with stannic chloride as catalyst, in the temperature range 0° − + 20° C, no polymerization of

* Translated for Rubber Chemistry and Technology by Malcolm Anderson from *Doklady Akademii Nauk S.S.S.R.*, Vol. 100, No. 2, pages 275–278 (1955).

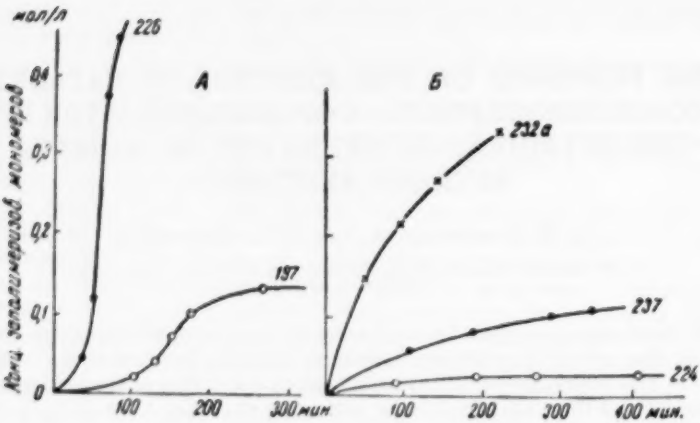

FIG. 1.—Polymerization as a function of time. The left-hand diagram shows the polymerization of butadiene and isoprene. The right-hand diagram shows the polymerization of butadiene and styrene. The abscissa indicates the time of polymerization in minutes; the ordinate the amounts, in moles per liter, of monomers polymerized.

butadiene takes place. To make the butadiene polymerization reaction go with this comparatively inactive catalyst, much higher temperatures are necessary. When a hydrogen atom on the second carbon atom is replaced by a CH_3 group, the reactivity of the diene molecules markedly increases: isoprene polymerizes with stannic chloride at 0° and −80° C. When relatively large amounts of butadiene are added to the isoprene (isoprene concentration, 15–20 mole-per cent), an increase of the initial and maximum speeds is noted (see Figure 1*A*), which is due to an increase of molecular weight and of the speed of initiation of isoprene polymerization. (Butadiene under these conditions does not form initial active centers.) The addition of relatively large quantities of butadiene to the styrene (styrene concentration, 20 mole-per cent) causes a lowering of the polymerization speed of the styrene (see Figure 1*B*). Along with this, the speed of initiation of styrene polymerization decreases as well. During radical polymerization, the addition of a second monomer does not affect the speed of initiation of the polymerization of the first component in the system.

We suggest that this feature of the kinetics of carbon-chain copolymerization is due to the fact that, in solutions of monomers, the catalyst exists in the form of complexes between it and the monomers.

The catalysts aluminum chloride, boron fluoride, and stannic chloride are good electron acceptors. Complexes between these catalysts and molecules which are electron donors are well known. Complexes between stannic chloride and various aryl-substituted ethylenes were investigated by Skraup and Freundlich[4].

TABLE I

Experiment no.	Initial concn. isoprene (moles/l.)	Initial concn. butadiene (moles/l.)	Concn. $SnCl_4$ (moles/l.)	Experiment no.	Initial concn. styrene (moles/l.)	Initial concn. butadiene (moles/l.)	Concn. $SnCl_4$ (moles/l.)
197	0.4074	0	0.0340	224	0.4842	2.25	0.0396
226	0.5661	2.718	0.0477	232a	0.5964	—	0.054
				237	0.5783	1.965	0.0990

In work which we carried out in 1945, we established that low molecular-weight polyisoprene and polyallyl chloride obtained from polymerization conducted in an ethyl chloride solution at $-20°$ C, in the presence of a high concentration of aluminum chloride, have a considerable amount of unsaturation. Analyses showed that the unsaturation of polyallyl chloride is connected with the splitting off of HCl molecules. The complexes formed here between aluminum chloride and low molecular-weight polymers of allyl chloride and isoprene are insoluble in hexane, but quite soluble in ethyl chloride and ether. In the presence of a solution of complexes between aluminum chloride and polyallyl chloride in ethyl chloride, no polymerization of the molecules of allyl chloride takes place, since these are of low activity in catalytic polymerization.

Isobutylene polymerized readily in the presence of these complexes. During this polymerization, the aluminum chloride migrated from the complex to the isobutylene molecule with the further formation of an active center. Isobutylene likewise displaced aluminum chloride from the rather stable complex which it formed with acrylonitrile (a complex with a 1:1 composition). In the presence of a complex between aluminum chloride and the low molecular-weight polyisobutylene polymers, allyl chloride polymerized; i.e., the aluminum chloride-polyisobutylene complexes were less stable than the aluminum chloride-polyallyl chloride complexes, and the molecules of allyl chloride displaced aluminum chloride from these.

We look upon the initiation in a catalytic polymerization as a reaction between the monomer-catalyst complex and the monomer.

The influence which one of the monomers in the system exerts on the speed of initiation of the polymerization of a second monomer is evidently due to the difference in stability of the complexes which are formed between the catalyst and the double bonds of these molecules. According to literature data[5], the stability of complexes between metal ions and unsaturated molecules depends on the number and structure of the substituents attached to the carbon atoms at the double bonds. It was shown that, as the number of substituents increases, the stability of the complex decreases, as a result of the existence of steric hindrances to its formation.

In the isoprene molecule, the two double bonds, which form complexes with the catalyst, differ from one another in that the number 2 carbon atom has an electropositive substituent, CH_3: $\left[\overset{1}{CH_2}{=}\overset{2}{C}(CH_3){-}\overset{3}{CH}{=}\overset{4}{CH_2}\right]$. The presence of two electropositive substituents on one of the carbon atoms which form the 1,2-double bond explains the low stability of its complex with stannic chloride and the high reactivity of this double bond. The complexes formed by the 3,4-double bond, on the other hand, are more stable; however, this double bond has a low reactivity in catalytic polymerization.

In the system, isoprene-catalyst, the equilibrium should be shifted to the side of formation of more stable complexes with the 3,4-double bond of isoprene, a bond which shows a low reactivity in the polymerization initiation reaction. In the presence of butadiene, the dispersion of complexes among the monomers establishes a new equilibrium. The butadiene molecules form with stannic chloride complexes which are less stable than the complexes formed between the catalyst and the 3,4-double bond of the isoprene, since the presence of the CH_3 substituent on the second carbon atom of the isoprene molecule should increase the electron density at the 3,4-double bond.

Thus in the presence of large quantities of butadiene, the speed of initiation of isoprene rises as a consequence of the reaction of displacing stannic chloride from its complex with butadiene to the isoprene molecule at the 1,2-position, with the formation of an active center.

In the system styrene-butadiene, the stability of the complex between stannic chloride and butadiene is evidently greater than that of the complex with styrene. As was noted above, the butadiene molecule has a low reactivity in catalytic polymerization. Hence when styrene molecules collide with the stannic chloride-butadiene complex, the reaction of polymerization initiation does not take place, since the formation of the active center $\overline{SnCl_4}—CH_2—CH=CH—CH_2—CH_2—\dot{C}H—C_6H_5$ requires a considerable activation energy. Thus, in the presence of butadiene, the speed of polymerization initiation for styrene decreases. Therefore the fact that the speed of initiation in copolymerization is not equal to the sum of the speeds of initiation for the separate polymerizations under the same conditions may be explained by the difference in activity of the complexes formed between the catalyst and the various monomers in the initiation reaction.

The increase of the number of active centers with time, which was observed during the separate polymerization of isoprene and the copolymerization of isoprene and butadiene at 0° C, apparently depends on the individual characteristics of polymerization initiation with isoprene and on a possible change of the conditions of initiation in the course of the polymerization process. Because of the low polarity of the medium, in carbon-chain polymerization, the positive ion of the growing chain is always located in the field of the negative ion of this same chain. This is possible in the case where the short carbon chain of the initial active center contains not less than 4 carbon atoms. Thus, in the formation of an initial active center from molecules of the vinyl series and a catalyst, two molecules of monomer should take part; in the reaction of polymerization initiation for dienes (isoprene), one molecule can take part. Here the reaction of forming such an ionic pair in media of low polarity makes possible the solvation of the carbon ion formed from the monomer molecules. It is possible that the increase of the number of initial active centers with time depends on the formation of unstable complexes between stannic chloride and the internal double bonds of the polymer chain. The probability that an initial active center may be formed by a reaction between the weakly bonded or free stannic chloride, liberated in the chain scission reaction, and the molecule of isoprene, can be very good, if we take into account the fact that isoprene is capable of forming an initial active center through the reaction of one molecule of monomer with the catalyst; and if we also consider the high activity which the 1,2-double bond of the isoprene molecule has in the initiation reaction. However, in order to clarify the mechanism of this phenomenon, further experimental research is needed.

The characteristics which we found in the kinetics of separate polymerization and of copolymerization of monomers in a carbon chain are based on the specific ionic mechanism of the catalytic polymerization.

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MASTICATION OF RUBBER. II. INTERPOLYMERIZATION OF NATURAL RUBBER AND NEOPRENE ON COLD MILLING *

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INTRODUCTION

The softening of elastomers on cold milling results from scission of the polymer molecules by the applied shearing forces[1]. The ruptured chains are free radicals, which can undergo mutual combination, interaction with oxygen and various additives, and branching (grafting) on to other polymer molecules. A general method of producing graft and block interpolymers between elstomers is therefore indicated, namely, to cold-mill the polymers together in the absence of small molecules which can terminate the polymeric radicals in order that the radicals may cross-terminate or graft onto the polymer molecules of the other type.

A survey of several pairs of the commercially important elastomers, natural rubber, butadiene-styrene, Neoprene, and butadiene-acrylonitrile, has shown that cold milling does effect interlinking. Detailed results for the rubber-Neoprene system are reported in this communication.

Experimental verification of polymer interlinking was obtained from the solubility properties of the milled elastomers. Cold milling of Neoprene under nitrogen produces gel, whereas of natural rubber does not, but the milling of mixtures gives gels containing natural rubber. Also, the solubilities and precipitation of the milled mixtures cannot be accounted for by these properties of the individual polymers. Finally, Neoprene-natural rubber mixtures, after and not before cold-milling, can be cross-linked by magnesium oxide, with rubber bound into the vulcanizate.

EXPERIMENTAL MATERIALS AND METHODS

Elastomers.—Deproteinized crepe[2] (<0.1% N, acetone extract 1.55%, ash 0.1%) was extracted by hot acetone in a Soxhlet apparatus for 16 hours and dried under 10^{-2} mm. Hg pressure just before use. Neoprene of grade WRT was similarly extracted by methanol and dried (analysis: C, 53.3; H, 5.65; Cl, 40.0; ash 0.7%). Both polymers were wholly soluble in benzene. Mixtures of the desired proportions were blended by 5 passes through 12-inch rollers revolving at 18.7 r.p.m. with 0.005 inch clearance. Such mixtures behaved virtually identically on mastication with those obtained on freeze-drying benzene solutions.

Mixing method	Gel (per cent)	Swelling (per cent)	Neoprene in gel (per cent)
Mill blending	35	16	55
Freeze-drying	33	17	56

* Reprinted from the *Journal of Polymer Science*, Vol. 18, pages 129–140 (1955).

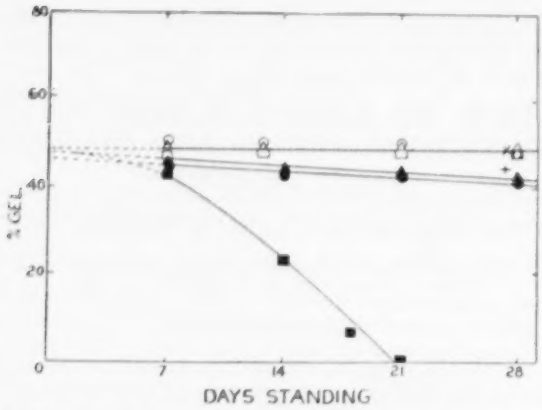


FIG. 1.—Rubber-Neoprene gels in benzene at different temperatures in air and under vacuum: (●) 25° C in air. (▲) 30° C in air. (■) 45° C in air. (○) 25° C *in vacuo*. (△) 30° C *in vacuo*. (□) 45°C *in vacuo*. (+) 30° C *in vacuo* in CCl_4 (×) 30° C *in vacuo* in $CHCl_3$.

Mastication.—An enclosed laboratory-masticator was used[3]. Three grams of mixed elastomers was milled in nitrogen in a 4-ml. volume between spiral scroll heads. The lower scroll rotated at 76 r.p.m., except when investigating variation of shear. Thermostatted water flow kept the average temperature of the masticating rubbers at 30° ± 2° C.

Gel on mastication.—Mixtures of undegraded rubber and Neoprene dissolved in benzene within two days. Mixtures that had been masticated in air dissolved more rapidly, going wholly into solution within a few hours. In contrast, mixtures that had been masticated in nitrogen contained a fraction of the polymers which was readily soluble, and a fraction which remained swollen with solvent but possessed sharp boundaries with the liquid phase.

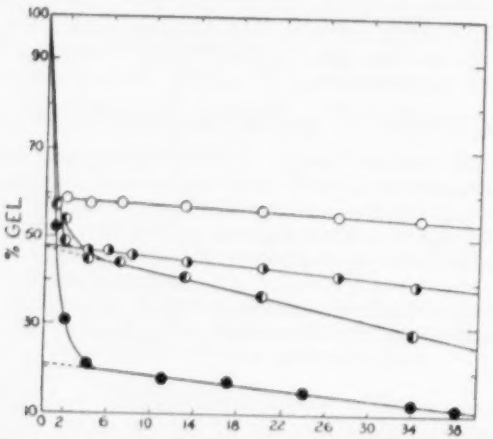


FIG. 2.—Degradation of gels in benzene under air: (○) Neoprene milled 100 min., (◑) 75% Neoprene/25% rubber milled 100 min., (◐) 50% Neoprene/50% rubber milled 60 min., (●) 25% Neoprene/75% rubber milled 20 min.

It had to be established that this insolubilization on mastication was the result of production of a chemical network, or gel, and not of a mere entanglement of polymeric chains. For this purpose, the stability of the gel with time in benzene was tested at three temperatures in the presence of air and on evacuating to $< 10^{-3}$ mm. Hg pressure, and the gel content in benzene compared with that obtained in carbon tetrachloride and chloroform (Figure 1). Total dissolution of gels floating in carbon tetrachloride and chloroform in the presence of air occurred within 28 days. The rapid dissolution to constant gel content in the evacuated samples shows the reality of the gel, and is inconsistent with a disentanglement interpretation. Further, these gels had compositions within the narrow range of 71–73 per cent Neoprene, whereas the samples in air diverged from this composition to greater than 80 per cent Neoprene after 28

TABLE I

Initial per cent Neoprene	Minutes of mastication	Per cent Neoprene in gel on standing					
		2	4	7	13	20	27 days
75	100	88	89	—	90	89	88
50	60	58	62	—	—	72	77
25	20	29	—	31	35	—	41

days in benzene at 25° C. Gel swellings in air also increased from the constant value of 14 obtained with the evacuated samples to 20 after 21 days at 45° C.

In order to standardize determination of gel contents without rigorous exclusion of air, gels of a range of composition were kept for varying times in benzene (Figure 2). In all cases, dissolution of the sol fraction was sensibly complete within four days, and thereafter gel content decreased slowly. The fraction of Neoprene in the gel increased on standing, as illustrated by the data in Table I.

The following technique for gel determination was adopted. Samples of milled elastomers of approximately 0.25 grams were immersed in 25 ml. of benzene in 1-inch diameter test-tubes closed by ground-glass stoppers and kept for 5 days at 30° C, with occasional inverting. The sols were decanted through lens tissue, 10-ml. portions of the filtrates in conical flasks were evaporated

TABLE II

Series	Per cent gel						
a	22	30	35	36	42	51	61
b	20	26	33	40	40	48	56

down and dried to constant weight within four hours *in vacuo*. (Freeze-drying confirmed the reliability of this more rapid procedure.) Gel contents were calculated from sol concentrations. Gels were surface-dried by filter paper and were weighed swollen and after drying to give degree of swelling in gram of solvent per gram of dried gel, correction being made for soluble elastomer in the swollen gel. The composition of the dried sol, and hence of the gel, was determined by microanalysis for chlorine. Reproducibility of gel contents on repeat masticatations were within 5 per cent, as illustrated by the figures in Table II for gels varying in composition from 20–60 per cent Neoprene.

Selective precipitation of sol fractions.—Fractional precipitation of Neoprene and rubber by alcohols and ketones from benzene and chloroform solutions gave overlapping ranges of precipitation. An alternative method, termed here "selective precipitation", of demonstrating changes in solubility properties on

forming block or graft copolymers was therefore adopted. Conditions were chosen for the precipitation of only one of the elastomers, using a precipitant which was a solvent for the other elastomer. Evidence for interpolymerization was thereby gained when a proportion of an elastomer remained partially soluble under conditions where it would normally precipitate, or was precipitated under conditions in which the unmodified elastomer would have remained soluble.

TABLE III

Concentration of solution (% Neoprene)	[η]	Petroleum ether added (ml.)	15	20	35
1.00	1.08	% precipitated	90	92	97
1.00	1.08	% precipitated	92	95	96
1.00	0.47	% precipitated	81	87	92
0.75	1.08	% precipitated	91	95	95
0.50	1.08	% precipitated	89	92	96
0.25	1.08	% precipitated	76	90	91

Neoprene in 50:50 benzene:petroleum ether (b.p. < 40° C) was precipitated by further addition of petroleum ether. After the addition of an equal volume of petroleum ether, no significant increase of precipitate occurred. The average molecular weight and concentration of the Neoprene had only a small effect on the fraction precipitated. The data in Table III are typical for the precipitation of Neoprene from 25 ml. of solution. Mixtures with rubber yielded similar fractions of Neoprene precipitated, the identity of the precipitate as wholly Neoprene being established by analysis. At the onset of precipitation, a small amount of rubber was coprecipitated, but redissolved on further addition of petroleum ether:

Petroleum ether added (ml.)	7.5	10	15	20
Neoprene precipitated (%)	83	91	95	96
Rubber precipitated (%)	3	10	<0.5	<0.5

The selective precipitation of rubber was less quantitative than that of Neoprene. The solvent mixture chosen was 45:45:10 of benzene:methylethyl ketone:acetone, and methylethyl ketone was used as selective precipitant. The molecular weight had a marked effect on rubber solubility; the following results are of precipitations from 25 ml. of 1 per cent solutions:

[η]	Methylethyl ketone (ml.)	30	40	50	60	70
3.85	% precipitate	77	84	86	—	—
1.06	% precipitate	—	52	58	62	65

An initial coprecipitation of Neoprene occurred, as shown for a 50:50 mixture of elastomers:

Methylethyl ketone (ml.)	30	40	50
% Rubber precipitated	86	80	84
% Neoprene precipitated	14	2	3

For all the precipitations recorded later, at least two determinations were made with different amounts of precipitant in the range where further increase in precipitant caused no experimentally significant increase of amount of precipitate.

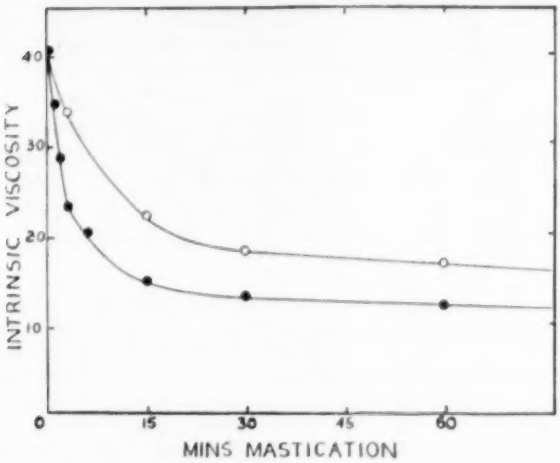


FIG. 3.—Intrinsic viscosity—mastication under air and nitrogen: (●) Milled under air, (○) Milled under nitrogen.

EXPERIMENTAL RESULTS

Viscosity changes on milling natural rubber under nitrogen.—The intrinsic viscosities of natural rubber decreased after masticating under nitrogen, although at a slower rate than on masticating in air (Figure 3). These viscosity changes were reproducible, and therefore not attributable to residual oxygen. The slopes of the viscosity-concentration curves yielded constant values of the Huggins' interaction constant[4], k', on masticating in air, and higher values on masticating in nitrogen (Table IV). Mastications up to 24 hours at rubber temperatures from 0 to 70° C gave no gels.

Gel on milling rubber-Neoprene mixtures.—The production of gel on milling rubber-Neoprene mixtures in nitrogen is illustrated in Figure 4. The properties of the gels are recorded in Table V. Neoprene remained wholly soluble for up to 40 minutes' mastication, after which gel was rapidly produced until it comprised 80 per cent of the elastomer after 2 hours' mastication. Increasing amounts of natural rubber, up to 75 per cent, reduced the period to the gel point to about 5 minutes. Gel increase after the gel point was slower than with Neoprene alone. The trend of gel swelling was to higher values with increase of proportions of rubber in the mixtures. Most critical evidence for

TABLE IV

INTRINSIC VISCOSITIES AND HUGGINS' INTERACTION CONSTANTS FOR DEPROTEINIZED CREPE MASTICATED IN NITROGEN AND IN AIR

Minutes of mastication	In air		In nitrogen	
	$[\eta]$	k'	$[\eta]$	k'
0	4.05	0.53	4.05	0.53
1	3.42	0.47	—	—
3	2.29	0.45	3.35	0.52
15	1.47	0.43	2.19	0.54
60	1.21	0.44	1.67	0.58
360	0.93	0.43	1.34	0.58
960	—	—	1.31	0.60

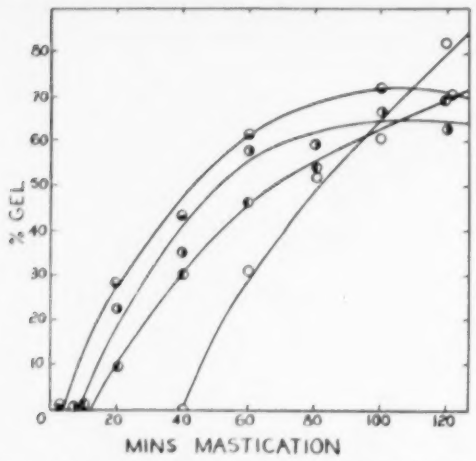


FIG. 4.—Gel contents on mastication of mixtures of rubber and Neoprene: (○) Neoprene, (◐) 75% Neoprene/25% rubber, (◑) 50% Neoprene/50% rubber, (◒) 25% Neoprene/75% rubber.

interpolymerization was the presence of appreciable amounts of rubber in these gels, in some cases considerably greater amounts than of the Neoprene originally present (Table V).

The data of Table V indicate that gel contents on prolonged mastication are less when rubber is present. This has been confirmed for a 50:50 rubber: Neoprene mixture, where gel contents reached an approximately constant level after 4 hours' mastication. The composition and swelling of the gel also did not vary systematically after this period of mastication:

Hours of mastication	1	2	3	4	6	9	12	16
% Gel	48	51	56	65	68	57	63	67
Gel swelling	14	14	13	14	17	15	13	—
Gel composition (% Neoprene)	57	58	61	60	59	64	63	64

TABLE V

GEL PROPERTIES ON MILLING RUBBER–NEOPRENE AT 30° C UNDER NITROGEN

Elastomer composition (% Neoprene)	Gel property	Minutes of mastication 20	40	60	80	100	120
100%	% gel	0	0	31	52	61	84
	Gel composition % Neoprene	—	—	100	100	100	100
	Gel swelling	—	—	18	14	11	3
75%	% gel	10	30	47	54	—	70
	Gel composition % Neoprene	57	71	85	86	—	85
	Gel swelling	51	20	17	16	—	9
50%	% gel	16	29	51	52	60	57
	Gel composition % Neoprene	23	60	56	60	60	61
	Gel swelling	39	15	13	13	18	13
25%	% gel	23	38	56	—	67	65
	Gel composition % Neoprene	29	24	26	27	27	28
	Gel swelling	57	20	23	19	13	7

TABLE VI

EFFECT OF RATE OF SHEAR ON GEL CONTENT
(Shear varied by speed of masticating rotor)

Minutes of mastication	% Gel with 50% Neoprene mixt.			% Gel with 75% Neoprene mixt.		% Gel with 100% Neoprene		
	76 r.p.m.	137 r.p.m.	380 r.p.m.	76 r.p.m.	137 r.p.m.	76 r.p.m.	137 r.p.m.	380 r.p.m.
20	16	33	34	10	31	0	0	87
40	29	38	42	26	39	0	0	88
60	51	51	61	47	73	31	38	92

The effect of rate of shear is as expected, i.e., gel forms more rapidly with higher rates of shear (Table VI). Gel compositions and swellings were similar to those in Table V at comparable gel contents.

Selective precipitation of sol fractions.—Selective precipitation of sol fractions from 50:50 rubber:Neoprene mixtures after different extents of mastication under nitrogen showed that the polymers had undergone modification affecting their solubility properties. Smaller fractions of the Neoprene in the sol became precipitated with the extent of milling under nitrogen, in contrast with the unaltered precipitation after milling in air (Figure 5). The visible characteristics of the precipitation of the sols also changed markedly. Solutions of unmasticated mixtures in 50:50 benzene:petroleum ether remained almost clear before and after precipitation of the Neoprene. The sol fractions of heavily masticated mixtures, however, were turbid even in 50 per cent benzene solutions and became so turbid with further additions of petroleum ether that precipitation could not be visually observed at any stage. Analysis of the precipitates revealed that no rubber was precipitated with the Neoprene.

On the other hand, selective precipitation of rubber in milled mixtures carried down appreciable amounts of Neoprene (Table VII). The rubber precipitations were complicated by the effect of the molecular weight on its solubility. Longer periods of mastication gave a decrease of rubber precipitated, perhaps ascribable merely to decrease of molecular weight. However, the

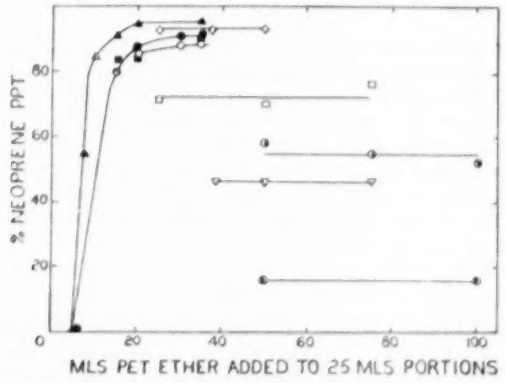


FIG. 5.—Selective precipitation of Neoprene with petroleum ether. Neoprene: (▲) unmilled, (○) highly degraded. Initial 50–50 Neoprene-rubber mixture: (◇) 2 hrs. in air, (●) 50 min. under N_2 (■) 1 hr. under N_2 (□) 2 hrs. under N_2 (▽) 6 hrs. under N_2 (◐) 12 hrs. under N_2 (◑) 12 hrs. under N_2 in Banbury.

TABLE VII

SELECTIVE PRECIPITATION OF RUBBER–NEOPRENE SOLS BY METHYLETHYL KETONE

Initial % Neoprene	Hours of mastication	Sol composition % Neoprene	[η] of sol	% rubber ppt.	% Neoprene ppt.
50	0 in nitrogen	50	1.07	65	3
44	0.83 in nitrogen	37	1.02	77	15
50	1 in nitrogen	48	1.00	69	14
50	2 in nitrogen	47	0.96	70	23
50	2 in air	50	0.78	64	2

differences in turbidity and precipitation after milling for 2 hours in air and in nitrogen were marked (Table VII).

Cross-linking of the Neoprene component of milled mixtures.—50:50 Neoprene:rubber mixtures were subjected to different extents of mastication in a laboratory-size Banbury mixer[1]: (1) masticating for 10 minutes under nitrogen to homogenize the two elastomers, with minimum degradation or other reaction; (2) masticating for 2 hours in air, with the temperature of the rubber raised to ~55° C by internal friction; (3) masticating for 12 hours under nitrogen with the temperature of the rubber at 60–70° C. The mixtures were then treated similarly to cross-link only the Neoprene component. The resulting networks contained bound rubber only after masticating under nitrogen (Table VIII).

TABLE VIII

SOL FRACTIONS OF 50:50 NEOPRENE:RUBBER MIXTURES CROSS-LINKED BY MAGNESIUM OXIDE

System	Minutes at 140° C	% soluble in		% Rubber bound in network
		Benzene	Petroleum ether	
(i)	40	50	49	0
(i)	120	48	47	<2
(ii)	40	55	53	0
(ii)	120	56	54	0
(iii)	40	37	35	28
(iii)	120	36	29	26

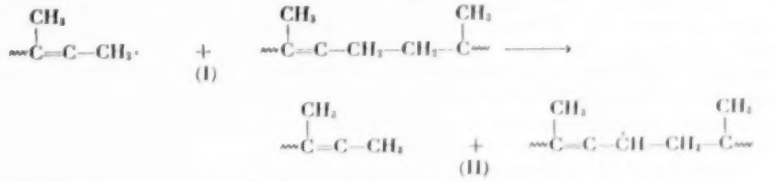
The recipe used for cross-linking only the Neoprene in 100 parts of elastomer mixture was 4 magnesium oxide, 5 zinc oxide, 0.5 stearic acid, and 1 hexamethylenetetramine. Cross-linking was carried out at 140° C for 40 and 120 minutes in a conventional rubber mold. Only the vulcanizate after nitrogen milling, mixture (3), retained the shape of the mold cavity and exhibited the elasticity of a typical vulcanized rubber. The vulcanized mixtures were suspended in benzene and petroleum ether for 7 days at 30° C, and the fraction of the elastomers in the sol was determined. Analysis confirmed that the sol fractions were only of natural rubber.

DISCUSSION

The compositions of the gels, the solubilities of the sol fractions, and the incorporation of rubber in the network on cross-linking the Neoprene by magnesium oxide provide strong evidence that graft and block copolymers of natural rubber and Neoprene are formed on masticating under nitrogen. These three topics are discussed in the following sections.

Branching and gelation reactions on mastication.—In earlier work, no marked changes in the solid or solution viscosity of the rubber were observed after masticating in nitrogen[1]. This was ascribed to predominant mutual combination of the radicals produced by shear. With the more efficient shear of the small masticator (or in a fully loaded Banbury mixer), the viscosity on milling under nitrogen decreased markedly (Figure 3). The additional mode of radical termination now becoming significant must be partly termination by other polymer molecules, since the higher value of the Huggins' interaction constant, k', on masticating in nitrogen compared with masticating in air denotes appreciable branching[4]. This branching process does not lead to gel formation within wide time and temperature range of mastication.

A chemical interpretation of this branching reaction is suggested from the known ease of abstraction of hydrogen atoms from rubber molecules by free radicals. If the primary radicals, e.g., I, formed by shear rupture are terminated not only by combination[5] but also partly by abstraction of α methylenic hydrogen atoms from rubber molecules[6], e.g.:



the secondary radicals, e.g., I, are likely to be terminated by combination with other primary and secondary radicals. In this way a trifunctional and tetrafunctional network is produced.

The following analysis[7] shows that this simplified mechanism should lead to gelation: Let p = the number of free ends of the initial rubber molecules, q_1 and q_2 = the number of trifunctional units and tetrafunctional cross-links, respectively, and α_1 and α_2 = the probabilities that a chain end is at a trifunctional or tetrafunctional cross-link, respectively. As one and two free ends are produced, concomitant with each trifunctional and tetrafunctional point, respectively;

$$\alpha_1 = \frac{3q_1}{p + 4q_1 + 6q_2} \quad \text{and} \quad \alpha_2 = \frac{4q_2}{p + 4q_1 + 6q_2} \tag{1}$$

gelation will occur[8] if:

$$2\alpha_1 + 3\alpha_2 \geq 1 \tag{2}$$

that is, if:

$$\frac{6q_1 + 12q_2}{p + 4q_1 + 6q_2} \geq 1 \tag{3}$$

The gelation condition of (3) can clearly be satisfied with continued mastication to attain required values of q_1 and q_2. Where tetrafunctional branching can be neglected compared with trifunctional, substitution of the value of $\alpha = 3q_1/(p + 4q_1)$ in Flory's analysis (Equations 5 and 12 of Flory[8]) of trifunctional branching gives the distribution of chains with respect to network complexity and molecular weight.

This mechanism of branching gives no change of number-average molecular weight. Osmotic molecular weights on masticating natural rubber under

nitrogen do, however, decrease[9]. Radicals produced by shear are then not exclusively terminated by combination or hydrogen transfer with polymer. The further termination is plausible by small amounts of oxygen or other adventitious radical acceptor. This may explain the absence of gel, since another term is introduced in the denominator of (3) for these free ends.

In contrast with natural rubber, Neoprene and most other common synthetic elastomers undergo gelation on masticating in nitrogen. An obvious chemical reaction which readily produces gel is the addition at double bonds of the Neoprene. Radical attack at the double bonds of Neoprene, but not of natural rubber, is not unlikely due to the enhancement of reactivity by the electron-releasing chlorine substituent, as exemplified among other cases by the ready polymerization of vinyl chloride compared with propylene.

Considering gelation of rubber-Neoprene mixtures on masticating under nitrogen, the several factors involved preclude a detailed discussion of mechanism. Three features of the over-all process may be interpreted qualitatively: (1) the higher amounts of rubber in the gels just after the gel point than at later extents of reaction; (2) the more rapid onset of gelation with greater amounts of rubber present; and (3) the attainment of a limiting gel content that is greater with increasing amounts of Neoprene. Features (1) and (2) are in line with the higher initial viscosity of rubber than Neoprene, its longer chain length, and more ready rupture by shear into radicals. Factor (3) is expected from the mechanism already discussed of a direct termination of a fraction of the radicals proceeding concurrently with gelation[10].

Solubility of the sol fractions.—The usual method of detecting graft or block copolymerization is by fractional precipitation with a precipitant capable of almost quantitative precipitation of both polymers and with a measurable interval in titer between the end of precipitation of one polymer and the beginning of precipitation of the second[11]. Graft polymers normally precipitate in this interval. It is not always possible to find suitable precipitants, as with the Neoprene-rubber system. Accordingly the method of selective precipitation was adopted. It has the advantages, at least with elastomer systems, of wide applicability and no precise adjustment of solvent composition.

Experience with fractional precipitation is that the noncopolymeric (free) fraction of the most insoluble polymer is first precipitated, and then there is a sharp change of solubility for copolymers with even a very low fraction of the more soluble polymer[12]. Similar findings have been obtained with selective precipitation by a precipitant which is a good solvent for the other polymer, as with petroleum ether as precipitant for Neoprene. No copolymeric material is precipitated, as shown by the absence of rubber in the precipitate. The petroleum ether can, therefore, be pictured as sufficiently solvating the rubber fragments to maintain the collapsed Neoprene chains in solution.

If a good solvent for Neoprene but precipitant for rubber had been found, a similar precipitation of only free rubber would have been expected (as will be reported later for rubber-butadiene-acrylonitrile systems using acetone). However, methylethyl ketone precipitates an appreciable fraction of the copolymeric Neoprene (Table VII). Methylethyl ketone is a poor solvent for Neoprene, and so presumably cannot solvate the Neoprene fragments to such an extent as to maintain the collapsed rubber chains in suspension. Estimation of copolymeric rubber is further complicated by the incomplete precipitation of free rubber by the ketone.

The amount of Neoprene in the copolymer is readily calculated. Control experiments have shown that 95 per cent of the Neoprene is precipitated by

petroleum ether, independent of both molecular weight and concentration within the ranges used. Therefore this small correction to the precipitation levels of Figure 5 give the fractions of free Neoprene.

Selective vulcanization of the Neoprene.—Prior graft-copolymer formation provides a means of incorporating natural rubber into the network on cross-linking only the Neoprene. The rubber is attached at only one end of each chain to the network. This unusual network structure may possess interesting physical properties.

SYNOPSIS

Graft copolymerization of rubber and Neoprene has been effected by cold mastication. Experimental evidence is based on the properties of the gels produced, solubilities of the sol fractions, and vulcanization of the Neoprene component by magnesium oxide. Mechanisms of branching and gelling of Neoprene and rubber-Neoprene systems are discussed. The utility of selective precipitation for the detection of graft polymers is outlined.

ACKNOWLEDGMENT

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X-RAY DIFFRACTION STUDIES OF CRYSTALLIZATION IN ELASTOMERS *

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GENERAL PRINCIPLES

The constancy of the total x-ray scattering by a substance, regardless of its degree of crystallinity, has been demonstrated theoretically and experimentally[1]. This principle forms the basis of current x-ray diffraction procedures for measuring the crystalline and amorphous fractions of polymers and other partially crystalline materials. Although the determination of the total crystalline and noncrystalline x-ray intensities is a formidable experimental operation, acceptable simplifications can be devised for most substances. For example, natural and synthetic fibers can be sampled in such a way as to randomize the orientations of the crystalline and amorphous regions, thereby making possible a satisfactory measure of the crystalline and amorphous x-ray scattering to be obtained from a single radial section over a limited angular range[2]. The amorphous fraction f_a of partially crystalline polyethylene can be measured directly by comparing the amorphous intensity of a radial section below $2\theta = 60°$ with that of a melted reference specimen. The crystalline fraction is then found by difference[3], $f_c = 1 - f_a$. A somewhat similar procedure is applicable to elastomers of technological interest because the completely amorphous reference specimens are available in the form of the unextended elastomers at room temperature. Thus, noteworthy success has been achieved in determining the amorphous fraction of natural rubber specimens by comparing the intensities of radial sections through the amorphous halo for the partially crystalline and totally amorphous specimens[4]. As in the case of polyethylene, the crystalline fraction is determined by the difference $f_c = 1 - f_a$. It should be emphasized that these investigations of natural rubber have made use of the additional assumption, evidently justified, that the properly corrected peak intensity of a radial section through the amorphous halo is proportional to the total amorphous x-ray scattering by the specimen.

Unlike the crystalline phase, the amorphous phase of an elastomer scatters x-rays coherently over the entire range of solid angles, 4π, which is to say, at all radial angles, 2θ, and at all azimuthal angles, β (refer to Figure 1). Hence, it is apparent that any useful method of measuring the amorphous intensity must confine itself out of practical necessity to some restricted angular range which can be shown to be, or with good reason assumed to be, representative of the whole. The principal amorphous diffraction halo, which is generated mainly by radial vectors between adjacent molecular chains in elastomers, is a suitable subject for measurement because its integrated intensity bulks so large with

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respect to the total amorphous scatter that the size of possible errors due to any lack of representativeness[4] is very limited, and, furthermore, it can be measured with much better accuracy than other portions of the amorphous pattern. On the other hand, it is important to remember that any preferential orientation of the molecular chains comprising the amorphous regions of an extended elastomer will produce an azimuthal redistribution of intensity in the amorphous halo. Such a development would obviously invalidate estimates of the amorphous fraction that are based on a radial section through the halo at only one azimuth. The measurements of crystallinity in natural rubber reported to date have depended tacitly or expressedly on the immutability of the amorphous intensity distribution when extension and crystallization take place. That this assumption is well founded has been confirmed by at least one precise experimental investigation[3].

Figure 1 gives the conventions to be employed in describing the sample orientation in relation to the diffraction pattern. With the extension axis vertical as shown, azimuthal angles on the diffraction pattern are measured

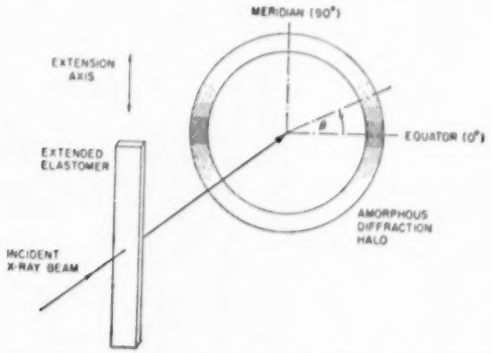

FIG. 1.—X-ray scattering by the amorphous phase of an elastomer.

from the horizontal axis, which will be designated the equator. The azimuth of the meridian, which coincides with the direction of extension, is then 90°. Figure 2 shows the x-ray diffraction patterns produced by a 5° C polybutadiene specimen at elongations of 0 and 535 per cent and at the temperatures 25° and −15° C. At 25° there is unmistakable evidence of molecular orientation in the form of an intensification of the amorphous halo at the equator. Microphotometer sections at various azimuths show the meridional intensity to be less than three fourths that of the equator. The absence of any crystalline diffraction effects confirms that this azimuthal redistribution of intensity is, indeed, the result of preferential orientation of the molecular chains in the amorphous regions. This intensity redistribution is also present, but less conspicuous, in the pattern prepared at −15° and 535 per cent elongation, which, in addition, contains the familiar doubled diffraction sickle on the equator produced by the oriented crystalline regions at moderate extensions[6]. At higher extensions the two components of the sickle coalesce on the equator. The unextended specimen at −15° C shows in addition to the amorphous halo a sharper Debye-Scherrer ring, which is produced by randomly oriented crystalline regions.

The photographic technique devised by Goppel[7] for measuring the crystal-

line and amorphous fractions in natural rubber, and subsequently improved by Arlman[8], equates the amorphous fraction to six experimental parameters:

$$f_a = \frac{1}{d'} \cdot \frac{I_a'}{I_s'} \Big/ \frac{1}{d} \cdot \frac{I_a}{I_s} \tag{1}$$

wherein primed and unprimed quantities refer, respectively, to partially and completely amorphous specimens. As this equation was employed by Goppel and Arlman, I_a is the peak intensity of the amorphous halo at a point unaffected by crystalline diffraction effects, and I_s is a measure of the intensity of the direct beam after transmission through the specimen of thickness d. For elastomers

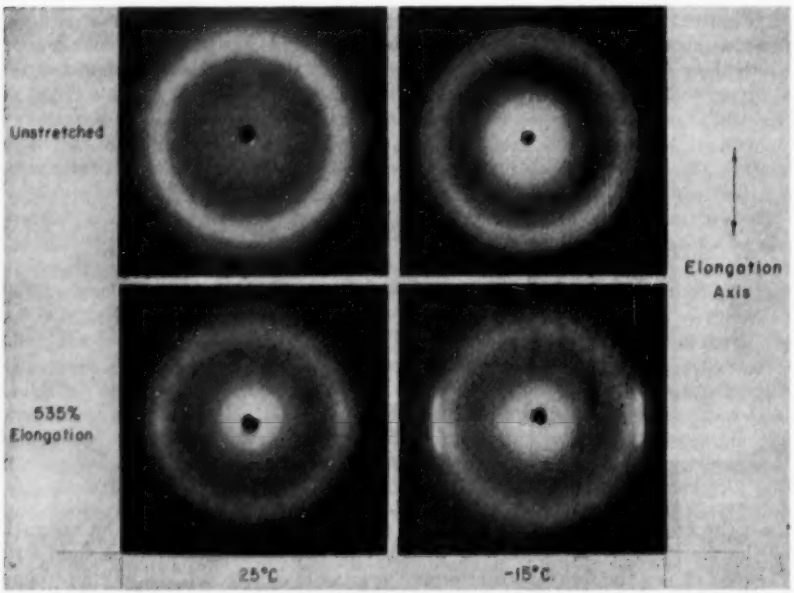

FIG. 2.—X-ray pattern of a 5° C polybutadiene specimen.

consisting principally of light elements ($Z \leq 8$) Equation (1) is theoretically accurate to within 2 per cent for typical experimental conditions. When applied to elastomers other than natural rubber, the possibility of preferential orientation of the molecules in the amorphous region must be recognized, in which case I_a must be re-defined as the integrated intensity of the amorphous halo. The necessity of employing this definition of I_a in the case of polybutadiene is attested by photographic diffraction evidence, as explained above. The remainder of this paper will deal principally with a study of preferential molecular orientation in polybutadiene and its bearing on the quantitative evaluation of crystallinity from diffraction measurements. Brief accounts will also be given of confirmatory measurements of crystallinity in natural rubber and of crystallite orientation in natural rubber and polybutadiene.

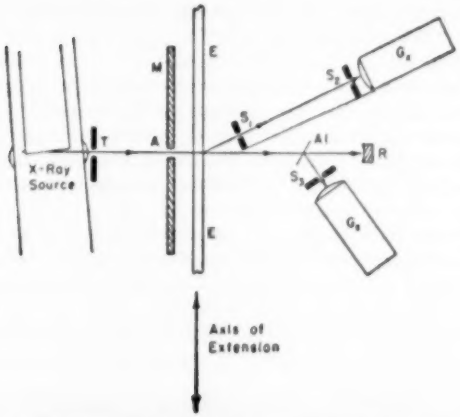

FIG. 3.—Schematic diagram of x-ray diffraction apparatus.

EXPERIMENTAL

Figure 3 is a schematic diagram and Figure 4 a photographic perspective of the Geiger-counter apparatus developed at Mellon Institute for making precise measurements of the intensities I_a, I_a', I_s, and I_s' of Equation (1). The necessary geometrical and mechanical features have been obtained by adding accessory devices to a standard Norelco wide-angle goniometer. The direct x-ray beam from a copper-target tube is defined by the $\frac{1}{4}°$ divergence slit T, and its vertical divergence[9] is limited additionally by the aperture A in the brass plate M, which shields the Geiger tubes G_a and G_s from unwanted radiation originating in the neighborhood of the x-ray tube housing. The beam penetrates the elastomer E, and x-rays scattered by the amorphous component are received by G_a. The specimen holder shown in these figures permits extension of the

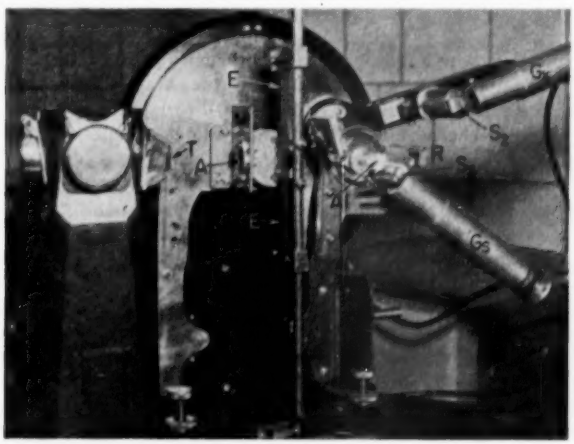

FIG. 4.—Perspective of x-ray diffraction apparatus.

elastomer in a vertical direction only, so that the amorphous intensity can be measured only on the meridian ($\beta = 90°$). The slits A and S_1 minimize the air-scattered x-rays that can be received by G_x. The direct beam, weakened by absorption in the elastomer, penetrates the reference sample of 0.002-inch aluminum foil, Al, and is then intercepted by the beam stop R. A diffracted ray from the foil is received by counter G_s, which provides a measure of the direct beam intensity after transmission through the elastomer, I_s or I_s'. Slits S_2 and S_3 are both equipped with nickel filters to remove the CuKβ component of the radiation.

The pulses from counter G_x are registered with a Tracerlab Superscaler Model SC-18 and those from G_s with the Norelco scaler. A special interconnecting timing circuit was incorporated to enable both units to register counts simultaneously for the same counting interval. It was found advantageous to set the control switch to shut off the counters when the standard counter G_s had counted a predetermined number of pulses, for example, 25,600. For the

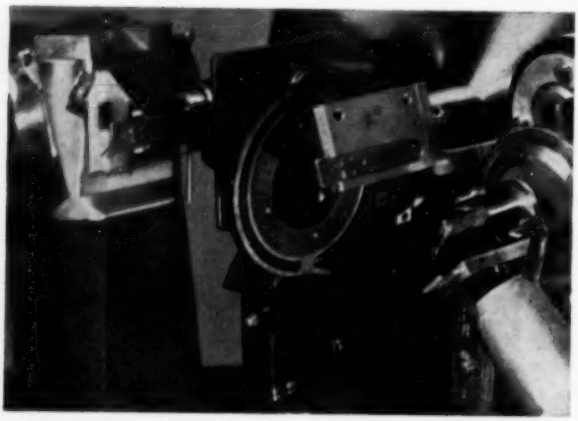

FIG. 5.—Close-up view of apparatus showing azimuthal specimen holder.

measurements at lowered temperatures, the entire sample and its supporting mechanism were enclosed in a windowless Styrofoam insulating box of such low density that the absorption of the direct and diffracted x-ray beams is unimportant. Air from the laboratory air line was passed successively through a drying column of silica gel, a flow meter, and a copper cooling coil immersed in a slush of dry ice and 1:1 chloroform-carbon tetrachloride in a Dewar, after which it was introduced into the cooling box through openings in both the top and bottom. By regulating the flow rate, any temperature down to $-40°$ C could be maintained for several hours with a mean variation not exceeding $\pm 1°$ C. The specimen temperature was measured with either a thermometer or a thermocouple.

Figure 5 is a close-up view of the goniometer, with an azimuthal specimen holder in place. This device, which was constructed in the shop by modification of an ordinary machinist's bevel protractor, permits rotation of an extended specimen about the axis of the direct x-ray beam. The specimen is first elongated with the aid of the usual stretching device, after which a small extended section is clamped off in the azimuthal holder. Another insulating

box of appropriate dimensions for this specimen holder was constructed for the measurements at lowered temperatures.

Returning to the general Equation (1) for the amorphous fraction, we see that the net accuracy in f_a will be a function of the accuracies with which four intensities and two thicknesses can be determined experimentally. Experience in this laboratory has shown that the thickness ratio d'/d can with minimum error be equated to α^{-1} (α being the extension ratio) provided only that the specimen is supported so as to permit unconstrained, and therefore proportionate, diminutions in its thickness and width (*affine* extension). The intensities I_a and I_c are derived from the experimental counting rates by (1) correcting them for the dead time loss of the Geiger counter and (2) subtracting the components of intensity due to air scatter and general x-radiation. Correction (1) is made with the standard formula:

$$N = N_0/(1 - N_0\tau), \tag{2}$$

in which N is the corrected counting rate in terms of the observed rate N_0 and the effective dead time of the Geiger tube τ (2.5×10^{-4} sec. for the Geiger tube employed, Norelco type 62019, and a full-wave rectifying x-ray generator). The air-scattered component N_A is given by:

$$N_A = (N_A)_0 \times \frac{N_c}{(N_c)_0} \tag{3}$$

$(N_A)_0$ and $(N_c)_0$ being, respectively, the dead-time corrected counting rates of counters G_c and G_c with no elastomer sample and N_c being the G_c counting rate with the sample in place. Because of the low sensitivity of the counter tubes for the general x-radiation, the correction for this component can be made adequately by measuring the diffracted intensity from the specimen after transmission through 0.35 mm. of aluminum, which removed more than 99 per cent of the CuKα radiation but only about 27 per cent of the general radiation[10]. The intensities I_a and I_c, when corrected as just described, permit the ratios I_a/I_c and I_a'/I_c' of Equation (1) to be determined with a probable error as small as 1 per cent when all the experimental conditions are optimum, including that at least 9000 counts be totalized in each measurement in order to keep the statistical errors of counting small. Considering the combined effect of the probable errors in the intensity and thickness ratios, it is possible to realize a net probable error in f_a of about ± 2 per cent. In order to achieve good relative accuracy in small values of the difference, $f_c = 1 - f_a$, it is evident that the greatest pains must be taken in the experimental measurements.

NATURAL RUBBER

A preliminary test of the equipment was made by applying it to the determination of crystallinity in natural rubber at room temperature as a function of extension. The specimen studied was smoked sheet purified and cross-linked with 0.6 per cent decamethylene *dis*-methylazodicarboxylate, using essentially the method of Flory, Rabjohn, and Shaffer[13]. Following the practice of the earlier investigators, the peak intensity of the amorphous halo at a single azimuth (90°) was accepted as being representative of the over-all amorphous intensity at the several extensions. The results are portrayed in curve A of Figure 6, which may be compared with the well-known curve of Goppel and Arlman, B[11], and recently published data of Nyburg, C[12], for natural rubber

specimens of somewhat different types. The three curves agree in failing to reveal appreciable crystallinity at extension ratios much less than 4.0, but they disclose minor differences in the progress of crystallization at the higher extensions.

MOLECULAR ORIENTATION IN POLYBUTADIENE

The samples studied were 2.5 × 10-cm. rectangular strips cut from a sheet of 5° C polybutadiene, 0.15 cm. thick, cross-linked with 0.6 per cent decamethylene dismethylazodicarboxylate. The extension ratios were determined by measuring the increase of separation of small India-ink fiducial marks initially placed 2 mm. apart along the center of the specimen strip.

Before any serious efforts could be made to pursue quantitatively the progress of crystallization in polybutadiene with reduction of temperature, it was necessary to evaluate the extent of molecular orientation in the amorphous state and, in particular, to establish that the quantity $(1/d') \times (I_a'/I_s')$ of

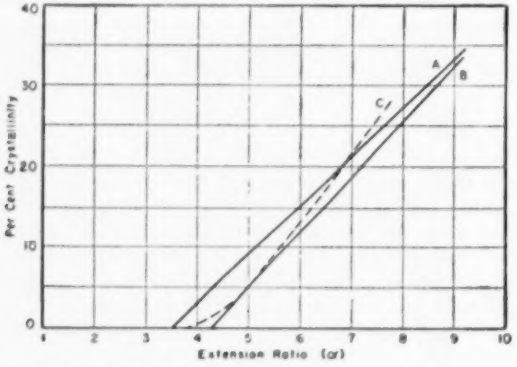

FIG. 6.—Crystallinity in natural rubber specimens at room temperature as measured by A, Alexander, Ohlberg, and Taylor; B, Goppel and Arlman[11]; C, Nyburg[12].

Equation (1) does, in fact, remain invariant when polybutadiene is extended at temperatures above the crystallization point. The demonstration of constancy in this quantity would be significant for two reasons. First, it would confirm that the integrated intensity of the amorphous halo is truly representative of the total amorphous scatter. Second, it would constitute a convincing argument for the applicability of Equation (1) to polybutadiene in extended states provided I_a and I_a' are defined as the integrated intensities of the halo for totally amorphous and partially crystalline specimens, respectively.

The intensity profile for an extension ratio of 6.1 was mapped out by taking peak intensity measurements at 10° intervals around the halo between azimuths of 0 and 90°, and by making radial sections at several azimuths in order to detect possible variations in the radial profile with azimuth. For the unextended specimen ($\alpha = 1$) only a single radial section was prepared, but peak intensities were measured at a number of azimuths to help average out any possible minor inhomogeneities in the sample. It was found for $\alpha = 6.1$ that not only the peak intensity, but the breadth of the radial sections and the radial angles of peak intensity as well, showed a dependence on azimuth. The salient numerical data are given in Table I. In interpreting these figures, it must be borne

TABLE I

PROPERTIES OF RADIAL SECTIONS THROUGH THE AMORPHOUS HALO OF POLYBUTADIENE FOR EXTENSION RATIOS OF 1.0 AND 6.1

		$\alpha = 6.1$	
	$\alpha = 1.0$	$\beta = 0°$	$\beta = 90°$
$2\theta_{max}$(°)	19.75	20.10	19.75
Equivalent R between molecular chains (A)	5.49	5.41	5.49
Integral breadth, W_i, of radial profile (°)	11.1	9.6	11.1
Relative peak intensity, I_{max}	1.00	1.62	0.98

in mind that the heightened equatorial intensity for $\alpha = 6.1$ results from an increase of the proportion of molecular chains that are oriented so as to approach parallelism with the extension axis.

The integral breadth of a radial profile is defined by:

$$W_i = \frac{\int I_{2\theta} d(2\theta)}{I_{max}} \tag{4}$$

As might be expected, for $\beta = 90°$ and $\alpha = 6.1$ the values of $2\theta_{max}$, R, and W_i agree with their values for the unextended elastomer. The highly oriented molecules are more densely packed than the unoriented, as evidenced by an average intermolecular distance of 5.41 Å for $\beta = 0°$ and 5.49 Å for $\beta = 90°$. This decrease of R is equivalent to an increased density of 3 per cent for the well-oriented regions of the amorphous phase. The decrease of integral breadth of the radial section through the halo at $\beta = 0°$ when extension occurs is indicative of a greater tendency toward discreteness in the distribution of the lengths of the intermolecular vectors about the smaller mean value of 5.41 Å.

Two independent measurements of the azimuthal intensity distribution in the amorphous halo at room temperature were made, the extension ratios being

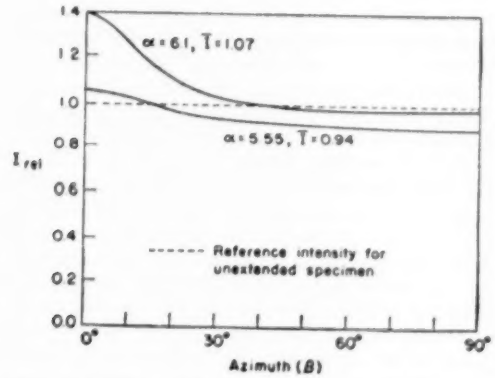

FIG. 7.—Azimuthal intensity distributions in the amorphous halo of extended polybutadiene specimens at room temperature.

5.55 and 6.1. The resulting curves are shown in Figure 7, wherein the quantity:

$$I_{rel} = \frac{1}{d'}\frac{I_a'}{I_r'} \Big/ \frac{1}{d}\frac{I_a}{I_r}$$

is plotted as a function of β. This expression has the form of Equation (1) for f_a in natural rubber, but it can now be equated to f_a only after integration over all azimuths, as explained earlier. At any particular azimuth I_a' is the peak intensity of the halo weighted by its integral breadth W_i. It is seen from the figure that the integrated intensities for the extended specimens agree with that for the unextended state to within 7 per cent, the deviation being positive in one instance and negative in the other. The quality of the agreement is not so good as might be desired, but, in view of the complexity and long duration of the measurements required to arrive at the integrated halo intensity, it was felt that these results tentatively establish the constancy of the integrated intensity with extension. Accordingly attention was next directed to the problem of measuring crystallinity in extended specimens at reduced temperatures.

CRYSTALLINITY IN POLYBUTADIENE

An important preliminary problem was to ascertain whether or not the intensity of the amorphous halo diminishes uniformly at all azimuths when crystallization occurs. Such proportionate reduction of intensity at all azimuths would be desirable from a practical standpoint because it would make possible quantitative evaluation of the amorphous and crystalline fractions by means of measurements at only one azimuth, for example, at the meridian. Such behavior, in addition, would point to a mechanism of crystallization that involves nonpreferential conversion of oriented and unoriented amorphous regions.

The following experimental procedure was followed. Prior to cooling, the specimen was stretched to the desired extension ratio α, mounted in the azimuthal holder, and its azimuth adjusted to some fixed value for the first series of measurements. The intensity ratio $(I_a'/I_r')_{t_0}$ was measured at $t_0 = 25°$, after which the specimen at the same extension and azimuth was enclosed in the insulating box and its temperature reduced to t_1 (usually about 10° C). An equilibration period of 30 minutes was allowed, and then the ratio $(I_a'/I_r')_{t_1}$ was measured until it reached constancy, which occurred within a few minutes except at low extensions. The temperature of the specimen was now reduced to t_2, a second equilibration period was allowed, and the ratio $(I_a'/I_r')_{t_2}$ was measured, and so on. The experimental results for three azimuths, 90°, 60°, and 30°, are plotted in Figure 8 for temperatures between +25° and −28° C. Confirmatory measurements are still required, especially at $\beta = 30°$, where the curve disagrees with the points for 60° and 90°, which are in mutual agreement. At $\beta = 0°$ the superposition of the halo by the crystalline reflections is so great (see Figure 2) that to date no precise measurements have been attempted at this azimuth. The x-ray data for $\beta = 60°$ and 90° indicate that crystallization in this specimen at an extension ratio of 5.55 begins somewhat below 0° C and increases rather linearly with further reduction of the temperature.

The foregoing results do not give a final answer to the question of whether or not the intensity of the amorphous halo diminishes proportionately at all azimuths when crystallization takes place, but the good agreement of the results at azimuths of 60° and 90° make an ultimate affirmative answer seem probable.

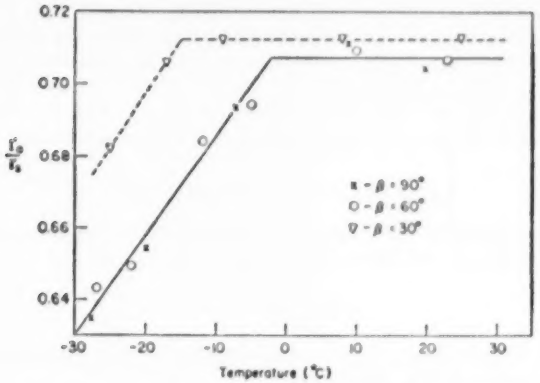

FIG. 8.—Amorphous halo intensity of polybutadiene vs. temperature at three azimuths. Extension ratio 5.55.

Further precise studies of the phenomena at $\beta = 30°$ and $0°$ are to be undertaken at an early date. Meanwhile tentative calculations of the crystalline fraction in polybutadiene at reduced temperatures have been made on the basis of simple meridional measurements of the intensity ratio I_a'/I_c'. When applied to the development of crystallinity resulting from reduction of temperature at a constant elongation, Equation (1) assumes the form:

$$(f_a)_t = \left(\frac{I_a'}{I_c'}\right)_t \Big/ \left(\frac{I_a'}{I_c'}\right)_{t_0} \tag{5}$$

Here t_0 is a temperature at which the extended specimen is presumably completely amorphous, such as 25° C for 5° C polybutadiene. The thickness ratio d_t'/d_{t_0}' is unity for all practical purposes and so may be disregarded. Table II gives the numerical results for two extension ratios, 4.38 and 6.13, and at several temperatures ranging from 25° to −16° C. The amorphous and crystalline fractions were calculated from the x-ray diffraction intensities using Equation (5) and the relationship $f_c = 1 - f_a$.

The crystallinity data of Table II are plotted in Figure 9, from which it is seen that (1) the crystalline fraction increases as the temperature is lowered and

TABLE II

CRYSTALLINE AND AMORPHOUS FRACTIONS AS A FUNCTION OF TEMPERATURE FOR 5° C POLYBUTADIENE HELD AT FIXED EXTENSIONS

Extension ratio, α	Temp. (° C)	Amorphous fraction, f_a	Crystalline fraction, f_c
4.38	25	1.000	0
4.38	9	0.966	0.034
4.38	0	0.952	0.048
4.38	− 5	0.906	0.094
4.38	−16	0.868	0.132
6.13	25	1.000	0
6.13	10	0.934	0.066
6.13	0	0.924	0.076
6.13	−10	0.885	0.115
6.13	−16	0.821	0.179

(2) the crystallinity at a given temperature increases with increasing elongation. In consideration of the experimental error limits discussed earlier, it must be recognized that the linear form of the curves indicated in the figure is somewhat tentative, especially at the lower crystallinities. However, the measured crystalline contents of about 13 and 18 per cent at $-16°$ C for extension ratios of 4.38 and 6.13 may be regarded with confidence.

CRYSTALLITE ORIENTATION

The birefringence of the crystalline phase in an elastomer in which the crystalline regions are preferentially oriented with respect to the direction of extension is[14]:

$$\Delta n_c = \Delta n_c^0 \cdot F \tag{7}$$

where Δn_c^0 is the birefringence of a single crystal of the crystalline phase and F is the orientation factor, defined by [15]:

$$F = 1 - \tfrac{3}{2}\langle \sin^2\gamma \rangle \tag{8}$$

The quantity $\langle \sin^2\gamma \rangle$ is the average value of the sine of the angle between the principal axis of a crystallite and the axis of extension. Taylor and Darin[14] have shown how Δn_c^0 can be calculated by combining appropriate x-ray and birefringence data, thus establishing a quantitative relationship between the observed birefringence and the crystalline fraction of an elastomer in extended states. The needful x-ray data are (1) values of f_a at some particular elongation and a series of temperatures and (2) a value of F under the same conditions. The determination of the amorphous fraction f_a has been discussed in the preceding section of this paper.

Reasonable assumptions concerning the distribution of orientations of the paratropic planes about the extension axis of an elastomer lead to the conclusion that Hermans' expression giving $\langle \sin^2\gamma \rangle$ for cellulose crystallites[16] can be applied to the crystalline diffraction sickle of polybutadiene almost unchanged:

$$\langle \sin^2\gamma \rangle = \frac{2 \int I(\beta) \cos\beta \sin^3\beta d\beta}{\int I(\beta) \cos\beta d\beta} \tag{9}$$

Here β is the azimuthal coordinate on the diffraction pattern as defined earlier.

The orientation factors of natural rubber and 5° C polybutadiene under different conditions were determined from x-ray diffraction patterns recorded on flat sheets of nonscreen x-ray film with nickel-filtered CuK radiation. A Leeds and Northrup recording microphotometer was used to measure the optical transmission values, which were converted to relative intensities by comparison with microphotometer traces of a graded density scale. The maximum intensities along the diffraction sickle concerned were plotted as a function of β, the background was subtracted, and the net intensities at small increments in β were used to compute $\langle \sin^2\gamma \rangle$ from Equation (9). The increments chosen were $\Delta\beta = 1°$ and $2°$, respectively, for natural rubber and polybutadiene.

Figure 10 is a plot of the azimuthal intensity distribution in the principal paratropic diffraction sickle of polybutadiene at $-25°$ C and an extension ratio

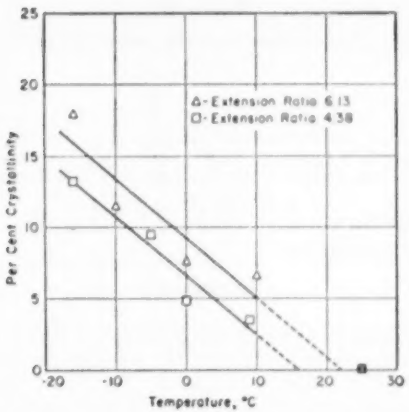

FIG. 9.—Percentage crystallinity in 5° C polybutadiene as a function of temperature for two extensions.

of $\alpha = 4.25$. It is interesting to note that at this extension ratio the point of maximum intensity does not fall at the equator but at about 10°. This means that the most probable mode of orientation is an inclination of about 10° to the axis of extension. Such an inclination is uncommon in crystallizable elastomers and does not occur in natural rubber.

Table III gives the results of the x-ray measurements for the specimens studied. The degree of orientation is very high in natural rubber compared with that in polybutadiene and, furthermore, it seems to be practically independent of the degree of extension. On the other hand, the degree of orientation in polybutadiene is less perfect, and there appears to be a dependence on

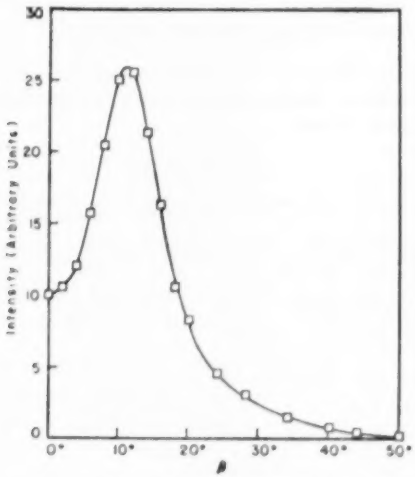

FIG. 10.—Azimuthal intensity distribution in the principal paratropic diffraction sickle of polybutadiene ($\alpha = 4.25$, $t = -25°$ C).

TABLE III

EXPERIMENTAL ORIENTATION FACTORS FROM X-RAY MEASUREMENTS

Specimen	α	t(° C)	$\langle \sin^2\gamma \rangle$	F
Natural rubber	5.0	25	0.0101	0.985
Natural rubber	7.5	25	0.0176	0.982
Polybutadiene	6.35	−15	0.1158	0.826
Polybutadiene	4.25	−25	0.1307	0.804
Polybutadiene	6.35	−25	0.1020	0.847

elongation, although the observed values of F do not differ by much more than the limits of experimental error.

SUMMARY

In general, extension of an elastomer results in a degree of preferred orientation of the molecular chains composing the amorphous phase. Therefore the amorphous fraction of a partially crystalline elastomer must be related to the integrated intensity of the amorphous diffraction halo rather than to the intensity at any one azimuth. A noteworthy exception is natural rubber, for which simple meridional measurements suffice.

A Geiger-counter apparatus, with beam monitor and temperature-controlling accessories, is described for making accurate measurements of the x-ray intensities scattered at any azimuth and at small or moderate Bragg angles. Measurements of crystallinity in natural rubber are in essential agreement with the findings of previous workers. When polybutadiene is extended at room temperature, molecular orientation occurs, but little if any crystallization. Measurements at lowered temperatures show that the crystalline fraction becomes appreciable at about 0° C and that it increases with further reduction of temperature and with increasing extension ratio. Preferred orientation of the crystalline regions in extended polybutadiene has been measured quantitatively with the object of providing jointly with birefringence measurements a value of the birefringence of a single crystal of polybutadiene.

ACKNOWLEDGMENTS

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INFLUENCE OF CRYSTALLIZATION ON THE SORPTION OF HYDROCARBONS BY NATURAL RUBBER AND GUTTA-PERCHA *

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It has been known that the mechanical properties and structure of amorphous and of crystalline polymers differ from one another sharply. However, the influence of the phase state of polymers on their thermodynamic properties has not been made clear. Hence it has been of interest to evaluate the effect of polymer crystallization on the polymer's sorption properties. For this purpose it was essential to compare the sorption properties of a polymer which can exist in either the amorphous or the crystalline state at the very same temperature. The most suitable material is natural rubber, which is capable of crystallizing either during prolonged aging or under stress and, therefore, may be obtained at the same temperature in both the amorphous and the crystalline states.

With the aid of a McBain balance in a high vacuum and under isothermal conditions[1], curves for the sorption of *n*-hexane by amorphous and crystalline samples of natural rubber at 0° and 25° C were obtained. In the experiment at 0°, the sorbent consisted of strips of natural rubber, some of which had been aged 8 months at 0° (the crystallized sample), and others aged for the same period at room temperature (the amorphous sample)[2].

In the tests at 25° C, natural rubber (smoked sheet) was used as the amorphous sample, while the crystalline sample was obtained by subjecting samples of natural rubber, heated to 80–90°, to a great stress, and then quenching them at 0° C. The content of crystallized phase in samples such as these is estimated as 30–35 per cent[2].

The experimental data in Figure 1 indicate that in both cases, at 0° and 25°, the isothermal curves of sorption by amorphous and crystalline natural rubber are roughly in agreement; i.e., the presence of the crystalline fraction does not change the sorption capacity of the rubber. (The curve obtained at 25° falls below that at 0° because of the increase of the mobility of the molecules at higher temperatures.)

Figure 2 presents isothermal curves at 25° for sorption on a crystalline sample of a purified and slightly vulcanized natural rubber which had been aged for 7 years at room temperature; and for amorphous samples obtained by the use of three methods given earlier: heating in air at 98° C for 7 minutes, heating in a vacuum at 70° for 6 hours, and repeated stretching.

The diagram shows that the sorption capacities of these natural rubber samples may all be represented by the same curve; i.e., the sorption properties of rubber do not depend on its phase state.

In the same diagram is shown the isothermal curve of the sorptionof *n*-hexane by gutta-percha (●), which is markedly different from the curves for natural

* Translated for Rubber Chemistry and Technology by Malcolm Anderson from *Doklady Akademii Nauk SSSR*, Vol. 99, No. 6, pages 1037–1039 (1954).

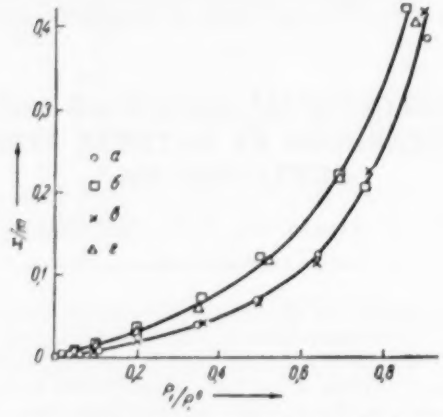

FIG. 1.—Sorption of n-hexane on amorphous and crystalline natural rubber at various temperatures. ○—Amorphous natural rubber, 0° C.; □—amorphous natural rubber, 25°; ×—crystalline natural rubber, 0°; △—crystalline natural rubber, 25°. The abscissa represents the ratio p_1/p_1^0; the ordinate x/t.

rubber, and attests to the considerably lower sorption capacity of gutta-percha. From the observed fact that the sorption properties of natural rubber are independent of its phase state, we surmised that the difference between the isothermal sorption curves for natural rubber and those for gutta-percha, which are *cis*- and *trans*-isomers, is based not on their phase state, but rather on a difference in the structure and flexibility of the chains. In order to check the accuracy of this proposition, a sorption experiment was set up for gutta-percha at 60° C, i.e., at a temperature above the fusion point of gutta-percha crystals[4], at which these are amorphous. With gutta-percha, it proved impossible to

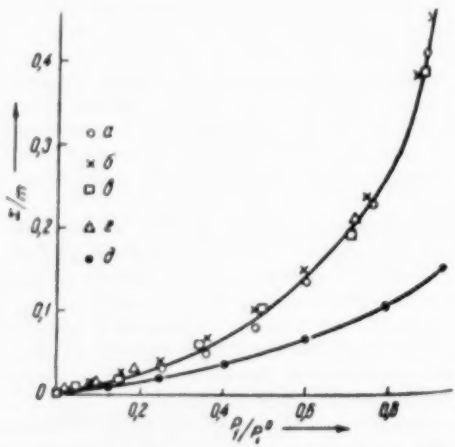

FIG. 2.—Sorption of n-hexane on amorphous and crystalline natural rubber and on gutta-percha. ○—Crystalline natural rubber; ×—heated in air at 98° C for 7 min.; □—heated in a vacuum at 70° for 6 hrs.; △—repeatedly stretched; ●—gutta-percha. The abscissa represents the ratios p_1/p_1^0, the ordinate x/t.

compare the sorption by amorphous and crystalline samples at the same temperature. Hence it was of interest to compare the sorption on gutta-percha with that on natural rubber, both of which were in the same phase state. A corresponding isothermal curve was therefore derived for sorption at 60° on amorphous natural rubber (see Figure 3). It follows from the diagram that the divergence between the sorption properties of natural rubber and of gutta-percha, noted at 25° C (crystalline sample) holds true also at 60° (amorphous sample), in both the sign and the quantity of the effect. Hence the sorption capacity of gutta-percha, too, is independent of its phase state, and is lower than that of natural rubber.

In this manner it was shown that the difference between the sorption properties of natural rubber and those of gutta-percha, which have the same chemical composition, results, not from their phase state, but from a difference in the structure of the chain molecules.

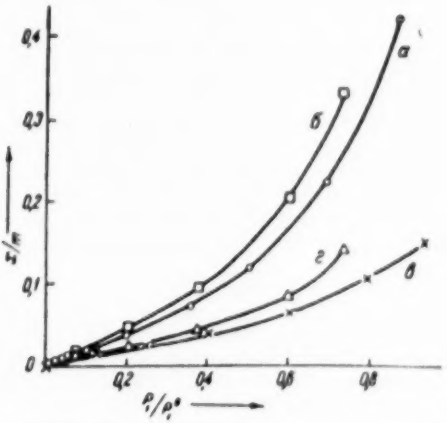

Fig. 3.—Sorption of *n*-hexane upon crystalline natural rubber and upon gutta-percha at 25° and 60° C. ○—Natural rubber, 25°; □—natural rubber, 60°; ×—gutta-percha, 25°; △—gutta-percha, 60°. The abscissa represents the ratio p_1/p_1^0; the ordinate x/t.

The results obtained were surprising. It had seemed as if the creation of crystals whose volume the solvent was incapable of penetrating, should reduce the sorption in proportion to the amount of the crystalline fraction formed, especially if one considers the fact that polymer crystals are incapable of permutoid swelling. But in actuality we see that the sorption capacity of a polymer does not change during crystallization, which attests to the absence of any crystalline formations with volume. This same conclusion was drawn earlier from purely structural observations[5].

In previous work it had been shown that the thermodynamic activity, and hence the sorption capacity, of amorphous polymers is determined by the elasticity of the molecular chains[6].

Inasmuch as the sorption of *n*-hexane on rubber does not change when it crystallizes or when the crystals are fused, we may safely draw still another conclusion, namely, that the crystallization of rubber causes virtually no change in its elasticity, nor, consequently, in the accumulation of configurations in its chain molecules. This circumstance also is in contradiction to the formation

of crystals with volume, in which the molecules should all have one certain configuration.

Thus, the formation of a new phase, although clearly detectable in structural and mechanical studies[7], has hardly any effect on the sorption properties of polymers. This indicates, not only that the crystals themselves have a peculiar structure, but also that it is necessary to examine more closely the very concept of phase conversions in polymers, a subject to which we shall turn in future communications.

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BIREFRINGENCE AND CRYSTALLIZATION IN ELASTOMERS *

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INTRODUCTION

It has been shown both experimentally and theoretically[1] that the stress-optical coefficient (the ratio of birefringence to tensile stress) in linear amorphous elastomers is a constitutive constant at small stresses. In partially crystallized elastomers, however, and in elastomers in which crystallization can be induced by stress, the birefringence is due, not only to the stress-optical properties of the amorphous phase, but is also due, and indeed significantly, to the birefringence of the oriented crystallites. This qualitative relation between excess birefringence and crystallinity in elastomers has been known since at least 1935[2]; however, to the author's knowledge, no quantitative statement of a relation between the birefringence, the degree of crystallinity, and the stress is available in the literature. It is the purpose of this paper to present a semi-theoretical relation of this sort and to show its applicability by comparing x-ray and birefringence determinations of the degree of crystallinity of stretched 5° C polybutadiene.

THEORY

In general, the optical properties of a medium are completely specified when the indexes of refraction along the mutually perpendicular principal axes, (x, y, z) are specified. To relate the optical properties of the medium to its constitution, it is assumed that the principal refractive indexes $n_i (i = x, y, z)$ are related to the principal components of the polarizability tensor, $A_{ii} (i = x, y, z)$, by the Lorentz-Lorenz relations:

$$(n_i^2 - 1)/(n_i^2 + 2) = 4\pi A_{ii}/3 \tag{1}$$

Then, using the approximation:

$$(n_z^2 - 1)/(n_z^2 + 2) - (n_x^2 - 1)/(n_x^2 + 2) = \frac{6\bar{n}\Delta n}{(\bar{n}^2 + 2)^2} \tag{2}$$

the difference in any two refractive indexes, which is called the birefringence, can be calculated from

$$\Delta n = \frac{2\pi}{9} \frac{(\bar{n}^2 + 2)^2}{\bar{n}} (A_{zz} - A_{xx}) \tag{3}$$

where $\bar{n} = (n_z + n_x)/2$ and $\Delta n = n_z - n_x$. If the medium is optically uniaxial, with its optic axis along the z axes, $A_{zz} = A_{yy}$, and it has one nonzero value for the birefringence. Stretched elastomers are uniaxial, with the optic axis along the axis of extension.

* Reprinted from the *Journal of Applied Physics*, Vol. 26, No. 9, pages 1075–1079, September 1955. The work was performed as a part of the research project sponsored by the Federal Facilities Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

To evaluate the polarizability tensor for a medium, it is generally assumed to be composed of n noninteracting elements per unit volume, small with respect to the wavelength of light, for which the principal polarizabilities and orientations are known or postulated. If the elements are uniaxial and are oriented with cylindrical symmetry about the z axis, the medium is uniaxial and the optical anisotropy can be shown to be:

$$A_{zz} - A_{xx} = n \int_0^{\pi} (1 - \tfrac{3}{2} \sin^2\gamma)(\alpha_{\parallel} - \alpha_{\perp})\rho(\gamma)d\gamma \tag{4}$$

where $\alpha_{\parallel}$ is the polarizability of the element along its optic axis, $\alpha_{\perp}$ is the polarizability of the element perpendicular to its optic axis, and $\rho(\gamma)d\gamma$ is the fraction of the elements in the medium oriented with their optic axis at an angle γ to $\gamma + d\gamma$ with the optic axis of the medium. In the special case where $\alpha_{\parallel} - \alpha_{\perp}$ is independent of the orientation of the elements, this reduces to:

$$\begin{aligned} A_{zz} - A_{xx} &= (A_{zz} - A_{xx})_0 F \\ F &= (1 - \tfrac{3}{2} \langle \sin^2\gamma \rangle_{Av}) \end{aligned} \tag{4a}$$

where $(A_{zz} - A_{xx})_0$ is the optical anisotropy which would be obtained if the elements were perfectly oriented, and $\langle \sin^2\gamma \rangle_{Av}$ is the average of the square of the sine of the angle between the optic axes of the element and the medium. F is called the orientation factor[3]. If the medium is composed of more than one type of element, the optical anisotropy can be written, under the above assumptions, as:

$$\begin{aligned} A_{zz} - A_{xx} &= \textstyle\sum_i (A_{zz} - A_{xx})_i f_i \\ \textstyle\sum f_i &= 1 \end{aligned} \tag{5}$$

where f_i is the volume fraction of i-type elements and $(A_{zz} - A_{xx})_i$ is the optical anisotropy pure i would have with the same angular distribution of elements as that (of i-type elements) existing in the composite medium. In rewriting Equation (5) in terms of the birefringence, if it is assumed that the function involving the mean refractive index in Equation (3) is the same in the separate phases, we obtain:

$$\Delta n_0 = \textstyle\sum_i f_i \Delta n_i, \tag{6}$$

where Δn_0 is the observed birefringence of the composite material, and Δn_i is the birefringence pure i would have in the same state of orientation.

To apply Equation (6) to polycrystalline elastomers, they are assumed to be composed of two types of elements; namely, very small crystallites, and amorphous chains. In this case, Equation (6) can be written in the form:

$$f_c = (\Delta n_0 - \Delta n_a)/(\Delta n_c - \Delta n_a) \tag{7}$$

where the subscripts c and a refer to the crystalline and amorphous phases, respectively. The birefringence of the crystalline phase can be written from Equation (3) and (4a), as

$$\Delta n_c = \Delta n_c^0 F \tag{8}$$

where Δn_c^0 is the birefringence of a pure crystal and F is the orientation factor, both of which can, in principle, be experimentally determined. To evaluate the birefringence of the amorphous phase, we must know something about the state of orientation of the amorphous chains. We adopt, as a working approximation, the assumption that, insofar as they affect the stress-optical properties of the amorphous phase, crystallites act only as additional cross-links.

This assumption permits us to evaluate Δn_a from[1]

$$\Delta n_a = cs \tag{9}$$

where c is the stress-optical coefficient of the amorphous material, and s is the tensile stress on actual cross-section. The critical point here is that the stress-optical coefficient is independent of the degree of cross-linking at low stresses and thus independent of the degree of crystallization.

GENERAL EXPERIMENTAL APPROACH

The general experimental procedure used for testing the relation between birefringence, stress, and crystallinity as given in Equations (7)–(9) was to measure the birefringence and stress on a lightly cross-linked specimen of 5° C polybutadiene held at constant length as the temperature was lowered from +30° to −30° C. The degree of crystallinity and orientation factor were obtained under the same conditions using x-ray diffraction techniques[4], and it was then determined whether the degree of crystallinity calculated from the birefringence stress data could be made to agree with the x-ray results using a single reasonable value for Δn_c^0, the birefringence of a single crystal of polybutadiene.

PREPARATION OF VULCANIZATES

The crude polymer (5° C polybutadiene prepared at the Government Laboratories, Akron, Ohio) was cleaned by alcohol precipitation of its filtered benzene solution after which it was dried in a vacuum at room temperature. The polymer was then redissolved in toluene with 1 per cent (based on polymer weight) of phenyl-2-naphthylamine added as antioxidant and the concentration (~5 per cent) was accurately determined by evaporating to dryness a weighed portion of the solution. The desired weight of cross-linking reagent, decamethylene dismethyl azodicarboxylate[5], dissolved in a little toluene was then added to the remaining weighed solution. The resulting solution was then transferred to 4 × 5 × 1-inch flat-bottomed glass trays, and bubbles and dissolved air were removed by placing the tray in a vacuum desiccator for 15 minutes. The solvent was then allowed to evaporate at room temperature and atmospheric pressure for 24 hours, after which the dry polymer sheet was heated to 60° C in a ventilated oven for 2 hours to complete the cross-linking reaction. The finished sheets were then stripped from the trays and stored under dry ice refrigeration until used.

MEASUREMENT OF BIREFRINGENCE AND STRESS

The specimens used for the measurement of birefringence and stress were small dumbbells 5.88 cm. in over-all length, 1.2 cm. long, and 0.25 cm. wide in the uniform central section, died from the sheets. The specimen thickness (0.005 to 0.015 inch) was measured to ±0.0002 inch with a dial micrometer, the length between India-ink fiducial marks placed about 1 cm. apart in the uniform central section was measured to 0.01 cm. with a cathetometer, and the specimen was clamped in place in the apparatus illustrated in Figure 1. The stretching device, illustrated in some detail in Figure 1(b), elongated the specimen without appreciably moving its center, through which passed the polarized light beam used in the measurement of the birefringence. The polarized light beam came through a small double-walled window in the rear of the working chamber. The birefringence of the specimen was measured with a Babinet compensator

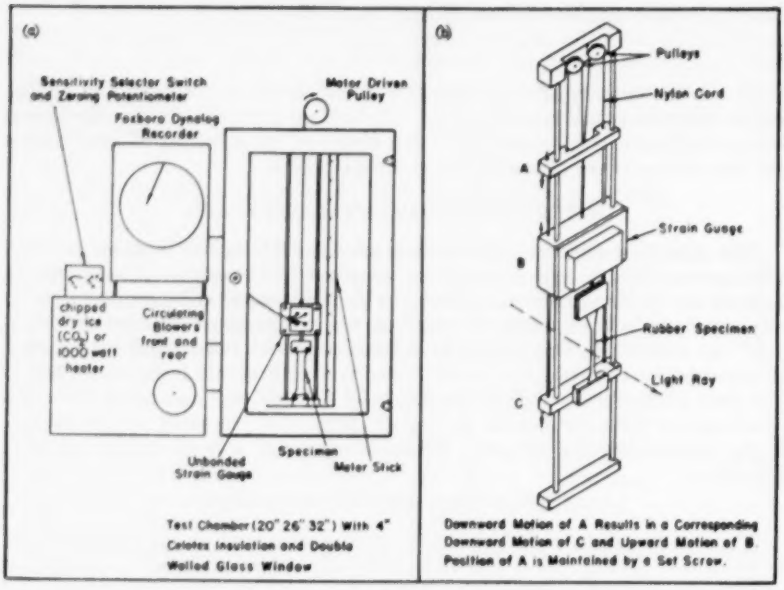
(a)
Sensitivity Selector Switch and Zeroing Potentiometer
Motor Driven Pulley
Foxboro Dynalog Recorder
chipped dry ice (CO_2) or 1000 watt heater
Circulating Blowers front and rear
Unbonded Strain Gauge
Specimen
Meter Stick
Test Chamber (20" 26" 32") With 4" Celotex Insulation and Double Walled Glass Window
(b)
Pulleys
Nylon Cord
A
Strain Gauge
B
Rubber Specimen
Light Ray
C
Downward Motion of A Results in a Corresponding Downward Motion of C and Upward Motion of B. Position of A is Maintained by a Set Screw.

FIG. 1.—Stress-birefringence apparatus.

mounted in front of the working chamber, and the stress was measured by an unbonded strain gauge [Figure 1(b)], the output of which was continuously recorded on a millivolt recorder. In calculating the birefringence and the stress, the thickness and cross-sectional area of the specimen were assumed to be $d_0/\alpha^{\frac{1}{2}}$ and A_0/α, respectively, where d_0 = initial thickness, A_0 = initial cross-section, and α = extension ratio; i.e., the deformation was assumed to be a constant volume affine extension.

Temperature control to $\pm 1°$ C was maintained by varying the speed of the blowers which cycled the working chamber air over chipped dry ice. In an attempt to approximate equilibrium conditions, each stretched specimen was relaxed for at least two hours at room temperature before cooling, and each fixed temperature was maintained until the birefringence and stress were approximately constant.

RESULTS

The birefringence and stress on actual cross-section as a function of temperature and extension ratio for 5° C polybutadiene cross-linked with 0.6 per cent decamethylene *dis*-methylazodicarboxylate are given in Table I. The fourth column in Table I, Δn_a, the contribution of the amorphous fraction of the specimen to the birefringence, was calculated from

$$\Delta n_a = (0.566 - 0.00356t)s \times 10^{-3}$$

t = temperature (° C)

s = stress on actual cross section (kg./cm.^{2})

The value $0.566 - 0.00356t$ for the stress-optical coefficient for amorphous 5° C polybutadiene was obtained from unpublished experimental data and is accurate from 0 to 50° C.

The degree of crystallinity can now be calculated from the data of columns two and four of Table I, using Equation (7), provided Δn_c^0 and the orientation factor are known. The orientation factor has been measured[4] at extension ratios of 4.25 and 6.35 and it was found to be a constant, within experimental error, with a mean value of 0.826 ± 0.020. Since, furthermore, the orientation factor is insensitive to small changes in the state of orientation, the quantity

TABLE I

BIREFRINGENCE, STRESS, AND PER CENT CRYSTALLINITY AT FIXED ELONGATION AS A FUNCTION OF TEMPERATURE FOR 5° C POLYBUTADIENE, CROSS-LINKED WITH 0.6 PER CENT DECAMETHYLENE *dis*-METHYLAZODICARBOXYLATE

Extension ratio	Birefringence ($\Delta n_s \times 10^3$)	Stress on actual cross-section (kg./cm.^{2})	$\Delta n_a \times 10^{3*}$	Percentage** crystallinity	Temp. (° C)
2.18	2.734	5.79	2.78	−.04	23.9
	2.975	5.79	3.04	−.05	11.6
	3.122	5.58	3.15	−.02	0.2
	9.109	4.59	2.74	5.00	− 9.2
3.472	6.957	13.90	6.63	0.27	25.0
	7.809	12.70	6.52	1.04	15.0
	9.359	11.98	6.55	2.28	5.3
	14.703	9.82	5.73	7.21	5.1
	19.558	6.23	3.86	12.44	−15
	25.532	1.20	0.81	19.12	30.1
	26.976	0.48	0.33	20.53	34.9
4.36	9.827	16.27	7.71	1.73	25.7
	10.997	15.06	7.73	2.67	15.0
	13.572	13.92	7.56	4.91	6.3
	17.271	12.09	6.99	8.35	− 3.5
	22.611	7.91	4.90	14.15	−14.9
	28.115	3.57	2.40	20.14	−30.0
	30.058	2.51	1.73	22.06	−35.3
5.88	13.364	23.05	11.02	1.96	24.6
	14.193	21.24	10.85	2.80	15.5
	17.702	19.08	10.44	6.07	5.3
	21.450	16.81	9.73	9.73	− 3.9
	28.268	12.83	7.92	16.65	−14.5
	33.048	7.61	5.12	22.34	−30.0
	34.911	6.47	4.48	24.23	−35.8
6.86	16.484	27.18	13.05	2.93	24.1
	17.331	24.93	12.74	3.91	15.3
	20.528	22.69	12.37	6.93	5.8
	26.273	19.82	11.63	12.35	− 6.0
	30.358	15.83	9.83	17.07	−15.8
	35.946	10.22	6.88	23.60	−30.1
	38.777	8.85	6.12	26.34	−35.1
7.77	18.785	33.78	15.37	2.98	31.1
	19.971	29.11	14.82	4.47	15.9
	23.720	27.19	14.74	7.78	6.7
	27.292	23.90	13.91	11.51	− 4.6
	31.845	20.82	12.80	16.24	−14.0

* The birefringence of the amorphous fraction.
** Calculated from $f_c = (\Delta n_s - \Delta n_a)/(0.130 - \Delta n_a)$.

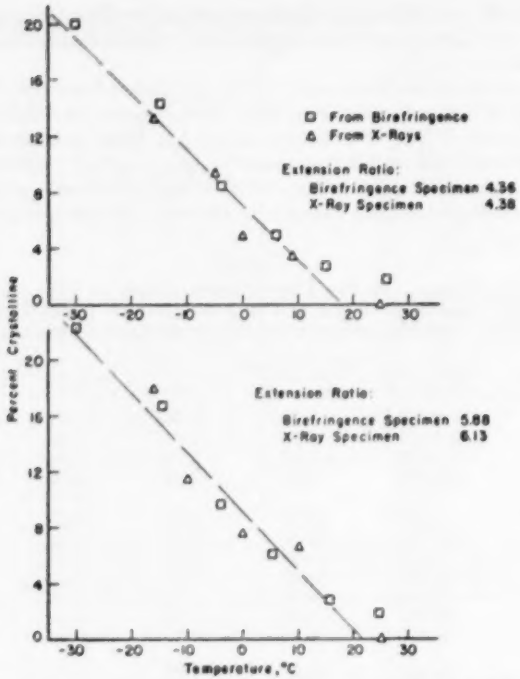

FIG. 2.—Percentage crystallinity vs. temperature for 5° C polybutadiene from x-ray and birefringence measurements.

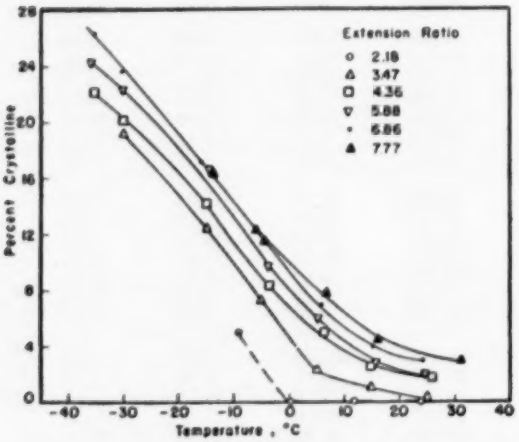

FIG. 3.—Percentage crystallinity vs. temperature for 5° C polybutadiene cross-linked with 0.6 per cent decamethylene dis-methylazodicarboxylate.

Δn_c can be treated as a constant (except possibly at very small extensions), which can be evaluated from a single known value of the degree of crystallinity. To this end we use the x-ray result[4] $f_c = 0.132$ at $-16°$ C at an extension ratio (α) of 4.38 in conjunction with the birefringence observations at $-14.9°$ C and $\alpha = 4.36$ to obtain the approximate value $\Delta n_c = 0.139$. Since this calculation puts too much emphasis on a single x-ray result, which may be in error by 0.02, it would obviously be more satisfactory to adjust Δn_c to obtain the best over-all fit with all of the x-ray data available[4]. When this is done, it is found that, with $\Delta n_c = 0.130$, the birefringence measurements agree with the x-ray measurements to the extent shown in Figure 2. This general agreement can hardly be considered a spurious result of a combination of x-ray and birefringence errors.

Making use of the value 0.130 for Δn_c, the degree of crystallinity as a function of extension and temperature has been calculated from the birefringence measurements. The results of these calculations are given in column 5 of Table I and in Figure 3. It is to be noted once again that these results are not purported to be true equilibrium values, although apparent steady states (on the time scale of the measurements) were attained.

DISCUSSION

In a test of the applicability of the proposed expression relating degree of crystallinity with birefringence, the principal points to be considered are the constancy and magnitude of Δn_c^0, the need of a correction for the contribution of the amorphous material to the birefringence, and the possibility of calculating this correction by the use of the stress-optical coefficient for the amorphous material. From the foregoing results, Δn_c^0 is satisfactorily constant, and its magnitude (0.157) is quite reasonable, since the theoretical value of Δn_c^0 for the closely related material, *trans*-polyisoprene, is 0.171 (see below). The need for an amorphous correction is evidenced by the magnitude of the corrections (see Δn_a in Table I) that were applied; and the fact that these corrections, calculated by use of the experimental stress-optical coefficient and the stress, yield satisfactory results, at least indirectly validates the procedure.

An interesting special case occurs when the birefringence measurements are taken under conditions of no stress. In this case, Equation (7) becomes

$$f_c = \Delta n_0 / F \Delta n_c^0 \tag{10}$$

Measurements of this type could be taken, for example, by stretching a specimen, freezing it, and observing the birefringence of the unclamped specimen at reduced temperatures. While we have made no measurements of this type, Treloar[6] has published density and birefringence data on natural rubber at 0° C under conditions such that Equation (10) should apply. He records values of the ratio birefringence to the increase in density (relative to the amorphous material) and finds that this quantity increases to a limiting value as the specimen extension is increased. This is exactly what Equation (10) predicts, for the crystallite orientation improves with extension and F approaches unity. Using his limiting value for the ratio, and assuming the density of crystalline natural rubber at 0° C to be 1.006 g./cc., the value of Δn_c^0 is found to be 0.218. It is possible to compare this figure directly with theory by calculating the birefringence of a natural rubber crystal (as a uniaxial crystal), using the crystal structure data of Bunn[7] and the bond polarizabilities of Denbigh[8] in conjunction with Equations (3) and (4a). The result, 0.215, is in remarkable agreement with Treloar's value. The figure

0.171 given previously for the birefringence of crystalline polyisoprene was similarly calculated using Bunn's structure data on gutta-percha[7].

It is interesting to note that attempts have been made to measure directly the birefringence of pure crystals of natural rubber and gutta-percha, using a polarizing microscope. The reported results are Δn_c^0 (natural rubber)[9] = 0.050, Δn_c^0 (gutta)[10] = 0.036. The discrepancy between these values and the calculated values is rather large; however, there can be little doubt but that the crystals studied experimentally were a more or less imperfectly oriented aggregate of submicroscopic crystallites and, hence, that a significant correction by way of the orientation factor is to be expected. Further serious doubt is cast on the experimental value 0.050 for natural rubber by the fact that Treloar records birefringence values for stretched partially crystalline natural rubber as high as 0.090, and we have observed values greater than 0.070.

SUMMARY

The semitheoretical expression:

$$f_c = \frac{\Delta n_0 - cs}{F\Delta n_c^0 - cs}$$

where f_c = volume fraction crystalline, Δn_0 = observed birefringence, c = the stress-optical coefficient, s = the stress on actual cross-section, F = a known function of crystallite orientation, and Δn_c^0 = the birefringence of a single polymer crystal, is proposed for relating birefringence, stress, and degree of crystallinity in polycrystalline elastomers under tensile stress. This expression is shown to yield results in substantial agreement with x-ray results for the degree of crystallinity of 5° C polybutadiene when $\Delta n_c^0 = 0.157$. Birefringence-density data on natural rubber (due to L. R. G. Treloar) are shown to be a special case of the foregoing expression, yielding a value $\Delta n_c^0 = 0.218$ for natural rubber, which is in good agreement with the theoretical value for this quantity.

ACKNOWLEDGMENTS

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INFLUENCE OF INTERMOLECULAR REACTION ON THE KINETICS OF SWELLING OF ELASTOMERS *

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The diffusion of a solvent through a high polymer is caused by the cumulative development of intermolecular forces and the action of the entropy factor[1]. Many authors have studied the state of equilibrium of a swollen high polymer in a solvent from this standpoint. The influence of the nature of intermolecular reactions on the kinetics of swelling, although indirectly recognized in some studies[2], has remained, on the whole, little investigated. One of the authors has developed a theory[3], according to which the closer is the value of the cohesive energy density of the polymer to that of the solvent, the greater is the rate of swelling.

Swelling of such substances as reprecipitated rubber or rubber from which the characteristics of a granular structure have been removed by processing, can be considered without reference to so-called intermicellar swelling. Swelling in this case is the result of the diffusion of solvent through the high polymer. Swelling of vulcanized rubber is accompanied by three-dimensional deformation. Three-dimensional deformation of rubber proceeds at a fixed rate. The rate of the relaxation process of three-dimensional deformation depends on the deforming force, the temperature, and the molecular reaction between the polymer and the solvent[4]. The force which causes three-dimensional deformation of a vulcanizate during its swelling performs the work of swelling, and can be determined from the value of the change of free energy or the thermodynamic potential.

The terms which describe the relations between the force of combination and the temperature and intermolecular interaction make up the equation which describes the change of free energy during swelling. It should be kept in mind that the force of combination does not remain constant during the swelling process; its value decreases as the system approaches equilibrium.

In the case where the rate of free diffusion of the solvent through the high polymer exceeds the rate of relaxation of three-dimensional deformation, the latter will determine the rate of the integral process. This can be expected either when the force of combination is small or when the high-polymer molecules are insufficiently elastic. If the molecular interaction between the combining components is slight, then the change of flexibility of the chain molecules during swelling can be ignored in first approximation. (It should be remembered that the intensity of the molecular reaction between the components is not determined by the heat effect of swelling, which, as Lipatov[5] showed, is an integral effect of several phenomena.) In this case, as was shown in a previous study[3], the rate of swelling can be expressed as follows:

$$\frac{dv}{dt} = \frac{\frac{v^2}{2} + \frac{v^3}{4} - \frac{\rho V_1}{Mv^{2/3}} - \frac{k-1}{2}v - \frac{V_1 E_\infty (v^{-4/3} - v^{-1})}{RT}}{\tau_1 \left(\frac{E'_0 V_1}{3RTv^{7/3}} + \frac{\rho V_1}{3Mv^{5/3}} + k - v - v^2 - 1 \right)} \qquad (1)$$

* Translated for Rubber Chemistry and Technology from the *Kolloidnyi Zhurnal*, Vol. 17, No. 1, 24-30 (1955).

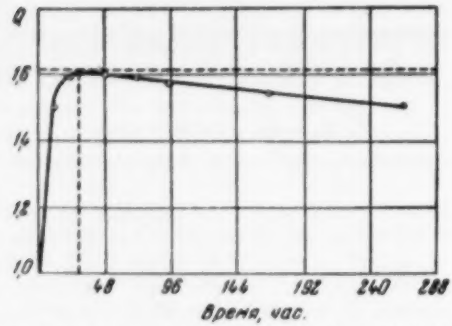

FIG. 1.—Kinetics of swelling of natural rubber in methylethyl ketone.
The abscissa indicates the time in hours.

where v s the volumetric fraction of polymer in the swollen gel; V_1 is the partial molar volume of the solvent; M is the molecular weight of a segment included between adjacent cross-links of the spatial network; ρ is the density of the polymer; k is a term comprising the molecular reaction of the components; E_∞ is the equilibrium high-elastic modulus; E'_0 is the initial elastic modulus; R is the gas constant; and T is the absolute temperature.

This equation was obtained by substituting the value of the combination force in the equation of the rate of relaxation of linear deformation. The force of combination, as has been mentioned above, can be determined from the work of swelling. When Equation (1) is applied, it is necessary to observe the limitations made previously.

In the case where the rate of three-dimensional deformation is not the slowest stage of the swelling process, the influence of the molecular interaction on the rate of spontaneous combination is determined by the relation of the coefficient of diffusion D to the activating energy of transfer E of a particle from one position to another.

$$D \approx \frac{d^2}{6\tau_0} e^{-E/kT}. \qquad (2)$$

where d is the order of distance between the particles; and τ_0 is the period of molecular vibrations.

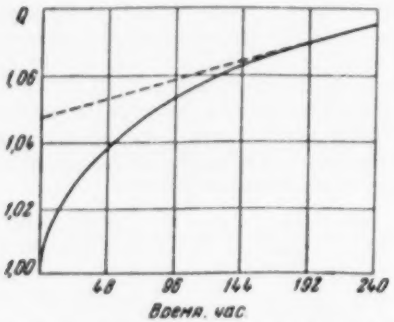

FIG. 2.—Kinetics of swelling of natural rubber in methyl alcohol.
The abscissa indicates the time in hours.

As Frenkel showed[6], the activating energy of transfer of a particle from one position to another bears a definite relation to the nature of the molecular reaction between the kinetic units (in this case—the segments of the polymer and the molecules of solvent).

Analysis of Equation (1) permits the following conclusion, which evidently can be applied beyond the limits of the assumptions made. The intensity and nature of the molecular interaction between the combining components is one of the factors which determine the rate of spontaneous combination of a high polymer and a solvent; the more intense is the molecular reaction between the combining components, the greater is the rate of spontaneous combination.

In the case where the mechanical properties of the high polymer are considerably changed by the combination, the influence of the intermolecular reaction on the rate of spontaneous combination remains effective, since the change of mechanical properties again appears as a result of intermolecular reaction. Comparison of the cohesive energy densities of the combining components makes possible a rough approximation in determining the intensity of intermolecular activity[7]. According to Equation (1), a decrease in the differ-

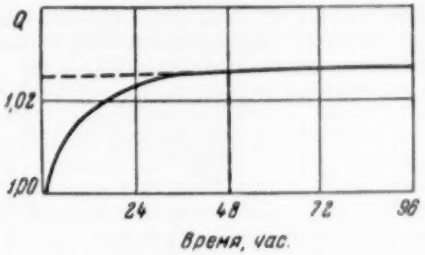

Fig. 3.—Kinetics of swelling of natural rubber in ethyl alcohol. The abscissa indicates the time in hours.

ence of the square roots of the cohesive energy densities of the components leads to a decrease of the parameter k and, consequently, an increase of the rate of swelling. To verify this, a number of experiments on swelling were set up. The kinetics[8] of the swelling of natural rubber in solutions with various intermolecular reactions is shown in Figures 1, 2, and 3. The solvents used—methylethylketone, methyl and ethyl alcohols—differed in polarity and in the values of the cohesive energy densities.

According to the results of the study of the influence of oxidation on swelling[9] the linear course of the kinetic curve of swelling is due to the influence of oxidation processes. Hence the equilibrium value of the degree of swelling (in the sense of swelling which is not complicated by chemical processes) can be obtained by extrapolating the linear relation of swelling to time toward the zero time value. The period in which equilibrium swelling is reached is determined by the period when the swelling time-degree of swelling relation become linear. For convenience we shall henceforth call this time interval t_p.

Examination of the data in Figures 1, 2 and 3 shows that, the more similar is the intermolecular action of the combining components, the sooner the equilibrium value of the degree of swelling is reached.

To illustrate the relation of the relative rate of swelling to the nature and intensity of the intermolecular action of the combining components, the values

TABLE 1

DEPENDENCE OF THE RELATIVE RATE OF SWELLING ON THE RELATION BETWEEN THE COHESIVE ENERGY DENSITIES OF POLYMER AND SOLVENT

Component	Density of specific cohesion energy (cal./cc.)	Difference between the square roots of the cohesive energy densities of rubber and solvent $(cal./cc.)^{0.5}$	Time of reach swelling maximum (hours) t_p
Vulcanized smoked sheet	65.5	—	—
Methylethyl ketone	85.	1.11	25.
Ethyl alcohol	161.	4.70	48.
Methyl alcohol	206.	6.26	192.

of t_p and the difference of the square roots of the cohesive energy densities of the solvents and the polymer are compared in the table.

The cohesive energy density of a soft vulcanizate of smoked sheet, determined by Gee's method, is 65.5 cal./cc.

The observed law—the decrease of the period at which the kinetic curve of swelling becomes linear with a decrease of the difference between the intermolecular activity of the combining ingredients—must have a parallel in the influence of temperature on the kinetics of swelling.

Vulcanizates of the following composition were swelled at various temperatures:

	Per 100 parts by weight of rubber	Per 100 parts by weight of rubber
SKS-30	100	—
SKN-26	—	100
Sulfur	0.5	0.5
Diphenylguanidine	0.3	—
Mercaptobenzothiazole	—	0.3
Zinc oxide	—	1.0
Vulcanization time	100 minutes	50 minutes

The kinetic curves of swelling of vulcanized butadiene-acrylonitrile and butadiene-styrene rubbers in dibutyl phthalate and dibutyl sebacate at different temperatures are shown in Figures 4, 5, 6 and 7. The rubbers were swelled in

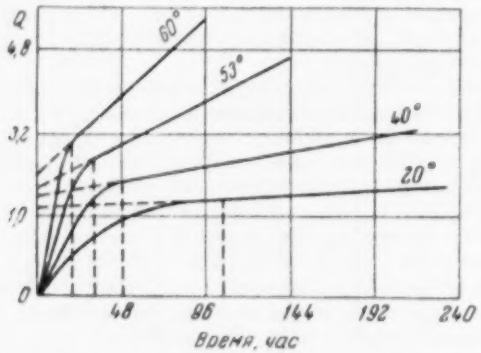

FIG. 4.—Kinetics of swelling of vulcanized butadiene-styrene rubber in dibutyl phthalate at various temperatures. The abscissa indicates the time in hours.

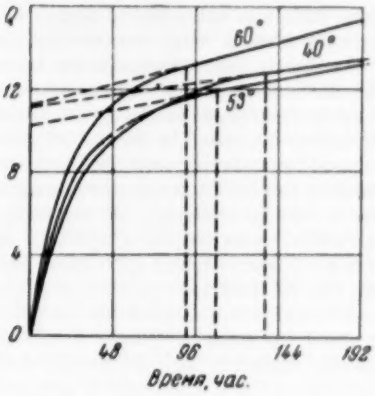

FIG. 5.—Kinetics of swelling of vulcanized butadiene-styrene rubber in dibutyl sebacate at various temperatures. The abscissa indicates the time in hours.

containers placed in a thermostat. The temperature variation was ±1° C. Swelling was measured by means of a torsion balance.

The kinetic curves of swelling in this case can also be divided in two parts: curvilinear and rectilinear.

The results presented in Figures 4, 5, 6 and 7 show an increase of the degree of swelling after a definite time interval with an increase of the temperature. For all the curves, an increase of temperature is accompanied by a decrease of the period necessary to reach the swelling—time maximum.

When vulcanized butadiene-styrene rubber is swelled in dibutyl phthalate, a linear relation between the degree of swelling and the time commences at 20° after 108 hours, at 53° after 30 hours and at 60° after 20 hours; for swelling in dibutyl sebacate, at 40° after 136 hours, at 53° after 108 hours, and at 60° after 90 hours. When vulcanized butadiene-acrylonitrile rubber is swelled in dibutyl sebacate, the linear relation between the degree of swelling and the time commences at 20° after 194 hours, at 53° after 156 hours, and at 60° after 108 hours; in dibutyl phthalate, at 20° after 456 hours, at 53° after 246 hours, and at 60° after 204 hours. An increase of the experimental temperature accelerates the swelling process. The smaller is the difference in the nature of the inter-

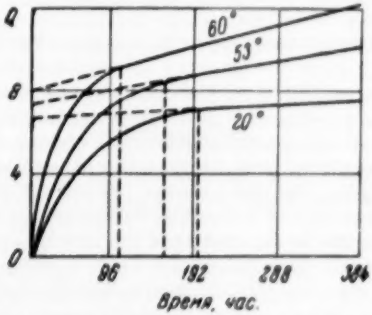

FIG. 6.—Kinetics of swelling of vulcanized butadiene-acrylonitrile rubber in dibutyl sebacate at various temperatures. The abscissa indicates the time in hours.

molecular forces (greater than the value of the degree of swelling), the more the temperature reduces the time in which the swelling maximum is reached. Thus, an increase of the experimental temperature from 53° to 60° during swelling of vulcanized butadiene-styrene rubber in dibutyl sebacate reduces t_p from 108 to 90 hours, and in dibutyl phthalate, by 10 hours. When vulcanized butadiene-acrylonitrile rubber is swelled in dibutyl phthalate in the same temperature range, t_p decreases by 64 hours, and in dibutyl sebacate by 38 hours.

To compare the absolute values of the rate of swelling, we shall consider the swelling of vulcanizates in dibutyl sebacate. In this case, the influence of the nature of the intermolecular forces on the kinetics of swelling is not overshadowed by the influence of intermolecular activity on the equilibrium degrees of swelling (accordingly for SKN-26 the equilibrium degree of swelling in the indicated temperature interval is ≈8 and for SKS-30, ≈10). The difference between the square roots of the cohesive energy densities of dibutyl sebacate and butadiene-acrylonitrile rubber is 0.65 (cal./cc.)$^{\frac{1}{2}}$, of dibutyl sebacate and

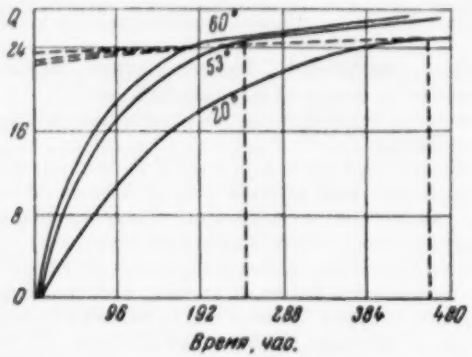

FIG. 7.—Kinetics of swelling of vulcanized butadiene-acrylonitrile rubber in dibutyl phthalate at various temperatures. The abscissa indicates the time in hours.

divinylstyrene rubber is −0.25 (cal./cc.)$^{\frac{1}{2}}$. Accordingly the times to reach the maximum degree of swelling at 53° are 150 and 108 hours, and at 60°, 108 and 90 hours.

Thus, the experimental data confirms the theory advanced above. The influence of the nature of intermolecular activity on the rate of swelling is demonstrated in all the experiments, the results of which are presented in Figures 1–7.

This theory is also confirmed by the results obtained by Ermolenko[10] in his study of the kinetics of swelling of loaded vulcanized natural rubber in a mixture of benzene and *p*-dichlorobenzene mixtures. Unfortunately, this study was made on a loaded vulcanizate, in which the effect of swelling of the high polymer may be suppressed by the reaction between the solvent and filler. Nevertheless, the kinetics of swelling of vulcanized rubber in mixtures of benzene and *p*-dichlorobenzene attests to the fact that the rate of swelling increases considerably in proportion to the accumulation of an ingredient which can polarize and react easily with the vulcanizate. Just as the addition of small amounts of a polar solvent to a nonpolar solvent at first increases swelling and solubility and reduces the molecular light-scattering effect, and a further increase of the

polar solvent content decreases swelling and solubility, so in this case it would be natural to expect an irregular change in the rate of swelling. However, this was not observed in the range of concentrations used.

When the polar solvent content of a mixture with a nonpolar solvent is small, the molecular action of the solution may resemble that of the polymer. Here the rate of swelling should increase according to Equation (1). After a composition is obtained in which the difference in the nature of the molecular activity of the solution and the polymer is minimal, further addition of a polar solvent will retard the rate of swelling of a nonpolar ploymer.

Comparison of the swelling of SKS-30 and SKN826 in dibutyl phthalate and dibutyl sebacate also indicates that the nature of intermolecular activity has a strong influence on the rate of spontaneous combination. The nature of the intermolecular activity of dibutyl sebacate is more nearly like that of SKS-30 than SKN-26. Consequently, the rate of swelling of SKS-30 in dibutyl sebacate is greater than that of SKN-26. Analysis of Equation (1) leads to the conclusion that the rate of swelling increases with an increase of the temperature.

We have already seen that the data in Figures 4, 5, 6, and 7 confirm this supposition: an increase of the experimental temperature from 53° to 60° reduces by 48 hours the time at which a maximum degree of swelling in dibutyl sebacate is reached in the case of butadiene-acrylonitrile rubber and by 18 hours in the case of butadiene-styrene rubber.

The case where an increase of temperature is accompanied by a retardation of swelling is theoretically possible. This will take place when destruction of the molecular bonds by heat leads to the formation of molecular groups which hinder comb nation; this is accompanied by an increase of the relaxation periods for three-dimensional stretching.

CONCLUSIONS

1. The kinetics of swelling of rubbers depends to a large degree on the intensity and nature of intermolecular activity.

2. A decrease of the difference in the cohesive energy densities of the combining ingredients, when the nature of their activity is the same, is accompanied by an increase of the relative rate of swelling.

3. An increase of the temperature in this case is accompanied by an increase of the relative rate of swelling.

ACKNOWLEDGMENT

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A THERMOCHEMICAL STUDY OF HIGH MOLECULAR WEIGHT COMPOUNDS *

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Among the classical methods which have found application in research on high-molecular compounds, the method of calorimetry is noteworthy. It is sufficient to mention the investigations into heat capacity[1], which, along with other measurements, helped to establish the second-order transition points, as well as the influence of crystallization temperature on the liquefaction of high polymers[2]. The determination of the heat capacity of isoprene and of natural rubber, in combination with data on their heats of combustion, permitted a calculation of the change of free energy of formation of natural rubber[3].

According to the data of Hock and Schmidt[4], the heat of swelling of natural rubber in various solvents ranges from +1.36 to −3.0 cal./gram. These data agree with those obtained from osmotic measurements[5]. Thus the change of free energy when natural rubber goes into solution is approximately determined by the entropy term; i.e., $\Delta F = -T\Delta S$. Bearing in mind that the heats of solution of rubber are of the same order of magnitude as the heats of mixing for two liquids, and are considerably lower than the heats of solution of solid bodies in liquids, we may conclude that the rubberlike state has more in common with liquid than with solid substances as regards solubility.

We must note, however, that not enough experimental research has yet been done on the heat of solution of rubberlike polymers to make possible any generalizations regarding all high-polymer compounds.

According to recently published data[6], the heat of solution of polystyrene in a 15-fold solution of the monomer equals about +8.2 cal./gram.

In a separate group are the investigations of the heat effects of various processes, both by means of combustion in a bomb calorimeter and by indirect measurements. To this group belong determinations of the heats of polymerization and of vulcanization, as well as the heat effects accompanying mechanical, thermal, and electrical treatment of high polymers and their solutions.

Results of determinations of the heat of combustion of vulcanizates of natural rubber[7] and of sodium-butadiene rubber[8] served in their time as important evidence that the vulcanization process was, in fact, a chemical reaction between rubber and sulfur.

The influence of mechanical treatment on the heat of combustion of high polymers was studied by us for natural rubber, sodium-butadiene rubber without antioxidants, and Vistanex. The data obtained are presented in Table 1 and Figure 1.

From the data presented, it follows that 10 minutes of milling reduces the heat of combustion of natural rubber by approximately 70 cal./gram, and that, within the limits of experimental error, the heat thereafter remains constant during milling for 3 hours on a roll mill. In the case of Vistanex, the heat of combustion is reduced by 71 cal./gram through milling for 1.5 hours. The

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TABLE 1

Time of milling (min.)	Natural rubber	Sodium-butadiene rubber		Vistanex		
	Heat of combustion (cal./g.)	Heat of combustion (cal./g.)	Data from elementary analysis (%)	Heat of combustion (cal./g.)	Intrinsic viscosity (η)	Data from elementary analysis (%)
0	10,789	10,641	H-10.83, C-86.35	11,208	—	—
5	10,723	10,698	—	—	—	—
10	10,714	10,622	—	11,206	11.04	H-14.61, C-85.67
15	—	10,595	—	—	—	—
20	10,712	10,576	H-10.77, C-86.72	11,183	8.98	—
30	10,717	10,518	—	11,170	7.79	—
50	—	10,620	H-10.57, C-85.59	11,160	7.15	—
60	—	—	—	11,151	6.84	—
80	—	10,560	—	—	—	—
90	—	—	—	11,137	6.34	H-14.66, C-85.31
110	10,702	10,434	H-10.31, C-82.00	—	—	—
125	—	10,286	H-9.89, C-81.91	—	—	—
180	10,724	10,175	—	—	—	—

intrinsic viscosity of solutions is diminished by a factor of 2 by this treatment. An analysis shows no appreciable degree of oxidation. The curve of change of the heat of combustion of unprotected sodium-butadiene rubber has a special character. At the outset a small rise is noted; then the curve declines to a value of about 120 cal./gram. According to data from elemental analysis during this period, no appreciable oxidation takes place. By further milling, the heat of combustion shows a sharp rise, which coincides with the oxidation

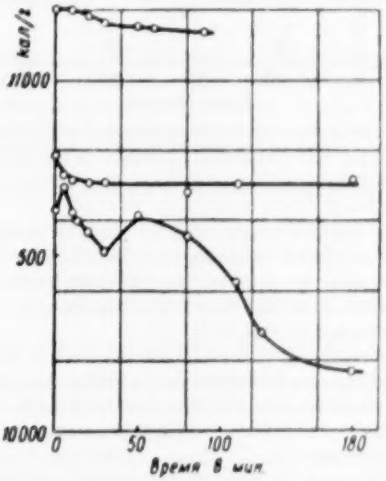

FIG. 1.—Effect of milling time on the heat of combustion of polymers. Bottom curve—sodium butadiene rubber. Middle curve—natural rubber. Top curve—Vistanex. The abscissa represents milling time in minutes; the ordinate the heat in cal./g.

of the rubber (about 1.2 per cent molecular oxygen) and then the heat drops steadily, at which time the oxygen content reaches 5.7 per cent. The data obtained permit us to assume that oxygen plays a special role in the milling process. In the cases of natural rubber, Vistanex, and the first stage of milling of sodium-butadiene rubber, oxidation does not occur, and milling is accompanied by disaggregation. Oxidation causes a linking of molecules on the one hand, and the formation of polar groups, on the other. As a result, rubber becomes brittle, crystalline, and insoluble in benzene. The increase of the heat of combustion, which coincides with the start of oxidation could be explained by the formation of especially activated oxygen compounds; the increase of the heat of combustion is too great, however, to be explainable by the formation of peroxides. This problem must be defined more accurately.

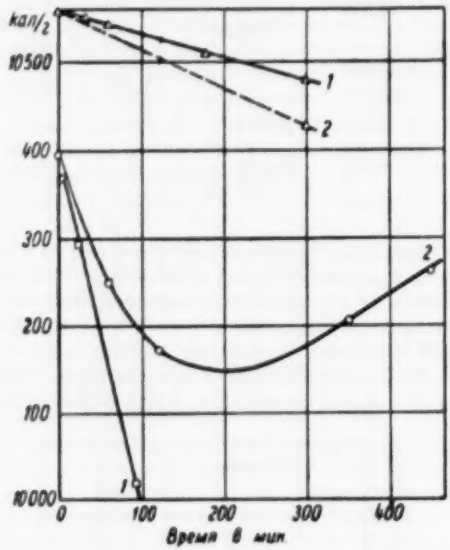

FIG. 2.—Effect of prolonged heating on the heat of combustion of sodium-butadiene rubber and Buna-S. Sodium-butadiene rubber—top curves: 1—Temperature of 250° C; 2—Temperature of 275°. Buna-S—lower curves: 1—Temperature of 130°; 2—Temperature of 150°. △ indicates Khokhlovkin data; □ and 0 data of Roth.

The abscissa represents the heating time in minutes; the ordinate the heat of combustion in cal./g.

A decrease of the heat of combustion of Buna-S during disaggregation at 130° and cyclization at 150° C was observed by Roth[9].

Together with Marya, we studied the effect of heating sodium-butadiene rubber in the absence of air at 250° and 275° C on its heat of combustion. The data obtained are depicted in Figure 2.

From the curves presented, it is seen that the heat of combustion of sodium-butadiene rubber undergoes a linear decrease during 5 hours' heating at 250° C. Since the rubber becomes insoluble during this treatment, we may assume that heating at 250° results in cyclization, which is accompanied by a decrease of the unsaturation of the rubber.

An analogous decrease of the heat of combustion, with a simultaneous loss of unsaturation, was observed[10] when 3–9 per cent solutions of Buna-S and natural rubber were processed under conditions where oxidation was excluded.

Determination of the heat effects of polymerization is possible by both direct and indirect means. While omitting for brevity any discussion of the great amount of experimental matter[11] in hand, we may note that the data obtained by both methods for the heats of polymerization of various unsaturated organic compounds fall within the range of 10 to 40 kcal./basic mole (i.e., per mole of monomer), while theoretical calculations[12] give in all cases approximately 20 to 24 kcal./basic mole.

It was natural that an attempt would be made to explain the reasons for this deviation from theory, and to apply this information to elucidate the structures of the polymers formed and also the mechanism by which they are formed.

It was shown[13] that heats of polymerization for the very same substance differ according to the conditions under which they are derived and the properties of the polymers formed. Thus, for instance, the heats of polymerization of

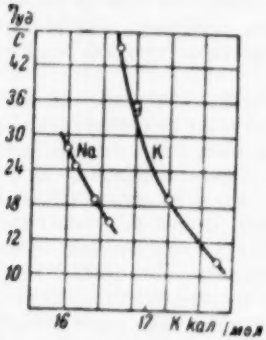

FIG. 3.—Polymerization of butadiene with sodium and potassium. The abscissa represents the heat of polymerization in kcal./base mole; the ordinate the ratio of specific viscosity to concentration.

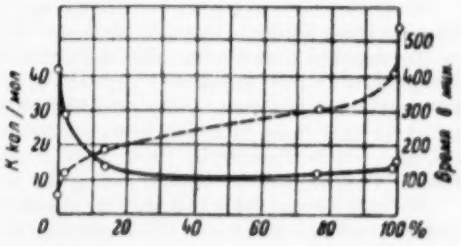

FIG. 4.—Polymerization of butadiene with sodium. The abscissa represents the per cent conversion of the butadiene; the ordinate on the left (corresponding to the solid line) represents the heat of polymerization in kcal./base mole; the ordinate on the right (broken curve) represents time of polymerization in minutes.

butadiene into various forms of polymers of approximately 17 to 30 kcal./basic mole were obtained. On the basis of the results derived, we noted the difference in structure of the polymers: and, in particular, the fact that the insoluble form of thermopolymer was the most saturated hydrocarbon.

Of considerable interest is the change of the heat of polymerization at various stages of the reaction, since such data might be useful in studying the mechanism of the reaction. For this purpose a direct measurement of the heat of polymerization in the diphenylmethane calorimeter[14] was undertaken, and it was established that the heat effect of polymerization decreases with an increase of the viscosity of solutions of the polymers produced. This relation is shown in Figure 3, where the abscissa represents the heat of polymerization in kcal./basic mole, while the ordinate represents the quantity $\frac{\eta sp}{C}$.

In the data of Luschinskii[15] on the determination of heats of polymerization from the heats of combustion for styrene and polymers of styrene with various viscosities, the same relation is found.

Besides this, we measured the heats of polymerization of butadiene in the presence of sodium at various stages of the process. The results are given in Figure 4, where the abscissa represents the percentage of the butadiene that has been polymerized, while the ordinate at the left represents the integral heat

effect in kcal./basic mole (for the solid curve), and the one at the right represents the time in minutes (for the broken curve).

The curve shows that the heat effect is distributed irregularly through the period of the process and thus cannot always be used directly for the study of the kinetics of the polymerization process.

Tong and Kenyon[16], using the slope of the curve for the dependence of thermal data on $t\sqrt{C}$ (where t is time and C is the concentration of benzoyl peroxide) obtained the value of 0.52 per cent/min. The corresponding kinetic data from the literature, with some extrapolation, gives the value 0.48 per cent/min.

We have no direct basis for converting the data obtained to the case of polymerization of compounds with only one double bond; however, the data of Luschinskii[15] for various heat effects with the unfractionated, precipitated styrene thermopolymer (10.6 and 13.8 kcal./basic mole), the data of Staudinger[17] (21.9 kcal./basic mole) and that of Goldfinger, Josefowitz, and Mark[18] (15.0 kcal./base mole) make it probable that no proportionality exists here between the total effect and the depth of the process.

From the curve in Figure 4 it can be seen, further, that at the first moment the heat effect amounts to about 40 kcal. This effect must be entirely related to the reaction between metallic sodium and butadiene, since this moment corresponds to only about 0.15 per cent of the whole polymerization. At 20 per cent polymerization of the butadiene, the heat effect reaches a value of about 11 kcal./base mole and remains the same until almost the end of the reaction. It is characteristic that at 99.6 per cent conversion the heat effect reaches 14 kcal./base mole, and during the last 0.4 per cent rises to 15.7 kcal.

We may assume from this that, at the end of the polymerization, some secondary reactions develop. The secondary reactions which take place toward the end of polymerization evidently are chemical in character and are connected with the complexity of the polymer molecule, as well as with the decomposition of the second double bond. The latter, in turn, is connected with the formation of rings. On the basis of the discussion above, we think that one might assume, however, that physical causes also play a part in the total polymerization effect.

According to the data given above, the heat effect decreases with an increase of the viscosity of solutions of the polymer. We established this relationship, not only for the case of direct measurements of the heats of polymerization for butadiene in the presence of alkali metals, but also for milling sodium-butadiene rubber (the first section of the curve) and Vistanex. Just such a relationship was observed in natural rubber during the first 10 minutes of milling. As was shown, this is confirmed by other work[15].

Tong and Kenyon[19] ascertained that the heat of polymerization of styrene and its products decreases with a reduction of the benzoyl peroxide concentration. It is possible that this relationship plays some part in the present case, since a reduction of the catalyst concentration generally means an increase of the degree of polymerization and, accordingly, the length of the molecular chains. Unfortunately, however, the authors made no viscosity measurements.

The examples cited compel us to recognize that such regularity has a general importance and depends neither on the chemical nature of the polymer nor on whether the samples investigated were obtained by means of polymerization, fractionation or depolymerization.

We think it reasonable to assume that, along with the chemical reasons for structural character, the phenomenon discussed has a considerable bearing on the difference in intermolecular forces between polymers. If this is so, one

may assume that, as the length of the molecular chain increases, the strength of molecular cohesion decreases.

Several authors[20], by means of a hypothesis[21] of steric hindrance brought about by the arrangement of the methyl groups in the polyisobutylene molecule, were able to explain the lower heat of polymerization of isobutylene (about 12 kcal./base mole). There is no doubt that this cause plays some part here, but it is evidently not the sole and decisive one.

In the opinion of Evans and Polanyi, the tetraisobutylene molecule does exhibit steric hindrance; however, according to the data we obtained, the heat of formation of tetraisobutylene from the monomer equals 19.4 kcal./base mole. Furthermore, the rise of the heat of formation from the monomer, from 12 to 16 kcal./base mole, which we derived from milling the polyisobutylene, is incomprehensible from the viewpoint mentioned. It is difficult to imagine that such profound changes might take place by milling as to bring about a removal of the steric hindrances. Likewise, from this point of view there is no explanation for the heat of polymerization of butadiene (about 11 kcal.), determined by us (Figure 4) in a polymer with no steric hindrances.

One of the component heat effects in the heat of polymerization is the difference between the heats of vaporization of the monomer and the polymer. An examination of the heats of vaporization of hydrocarbons shows that, based on the weight of the original unit, they decrease with an increase of the degree of polymerization until they reach a constant level. In particular, for lower molecular-weight polymers of isobutylene this limiting value is equal to about 3.5 kcal./base mole. On the basis of our hypothesis, one may assume that the heat of vaporization and the molar cohesion which is proportional to this (both calculated on the base mole) start to decrease again as the chain length grows further still. This conclusion is confirmed by the belief[22] that it is possible to lower the strength of the cohesion by having a large enough number of carbon atoms in the hydrocarbon chain.

One of the principal objections to the hypothesis which we propose is found in the heat of swelling of rubber, which was mentioned above. However, as we noted, this problem requires further work.

In order to verify the hypothesis which we put forward, we carried out the following experiments. Samples of polyisobutylene, unmilled and milled for 90 minutes, were placed in test-tubes in a bath of boiling water for several hours. After this, the first (unmilled) sample was cooled slowly over a period of hours, while the second (milled) sample was quenched by plunging it quickly into carbon dioxide at $-80°$ C. The molecules of the first sample, when cooled slowly (annealed), should have become arranged in a denser packing; while the shorter molecules of the second, when quenched quickly, should have become frozen in an irregular pattern. From the assumption which we present, one would expect that, as a result of such physical transformations, the heat of combustion of the first sample would have been lowered and that of the second increased. The results of the determinations confirm this expected effect. The heat of combustion of the first dropped by 45 cal./gram, while that of the second increased by 53 cal./gram.

In order to exclude the possibility of irreversible chemical reactions arising during prolonged heating, the following experiment was carried out. A sample of Vistanex, milled for 0.5 hour, was subjected by turns to annealing and quenching, and after each its heat of combustion was determined. The data obtained are given in Table 2; they show that the phenomena occurring during quenching and annealing have a physical character.

TABLE 2

Substance	Heat of combustion (cal./g.)					
	Milled 0.5 hour	Annealed	Quenched	Annealed	Quenched	Annealed
Vistanex	11,182	11,158	11,187	11,135	11,174	11,147
Vistanex	11,181	11,157	11,188	11,127	11,187	11,154
Vistanex	11,188	11,154	11,191	11,133	11,181	11,156
Vistanex	—	11,157	—	11,155	—	—

On the basis of this exposition, one may draw the conclusion that the heats of formation of high-polymer compounds result from the influence of several factors. The causes which have a bearing on the overall heat effect of polymerization are as follows.

(1) Variations in the mechanism of the reaction. We may note here that it is possible for diene compounds to combine in either the 1,2- or the 1,4-positions, while in the case of ethylene compounds, combination is possible either head-to-head or tail-to-tail, and also *cis-* and *trans-* forms may be present.

(2) The presence during polymerization of secondary reactions, such as branching and cross-linking, which may be accompanied by a decomposition of the second double bond and the formation of rings.

(3) A difference in the strengths of molecular cohesion in the polymers formed, which is related to the physical condition of the polymer, and which depends on the conditions under which it was produced and the way in which it was treated; there is also the relation to heat of polymerization, which depends on the length of the molecular chains.

In the process of polymerization, the rapidly growing molecular chains spread out chaotically in space. The degree of irregularity in the polymer molecules depends, on one hand, on the chemical structure of the molecules and, on the other, on the length of the chains formed. Short, more mobile chains go more easily into the irregular condition than do the long ones. The approximate determinations that we carried out showed that the sample of Vistanex milled for a long time exhibited the quenching effect to a lesser degree, which is entirely explainable by the greater mobility and the ability of the molecules to become oriented quickly in shorter chains.

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THE COMPARATIVE DETERMINATION OF THE MOLECULAR WEIGHT OF RUBBER BY THE METHODS OF LIGHT-SCATTERING AND OSMOMETRY *

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THE LIGHT-SCATTERING METHOD

One of the more recent research methods for high-polymer substances is the determination of molecular weight according to the diffusion of light in a solution. This method was successfully used by Debye[1] for determining the molecular weights of polystyrene and of polyvinyl esters, and by other investigators[2] for determining the molecular weights of polystyrene and of cellulose acetate. It seemed interesting to put this method into practice in our own investigation of the properties of rubber, which occupies one of the most important positions commercially among the high polymer substances.

The theory of light-scattering by pure liquids and solutions was developed by Einstein and Smoluchovskii[3] on the basis of the concept that the optical non-homogeneity of a liquid is the result of thermal fluctuations of density and concentration. The final results of Einstein's thermodynamic calculations may be presented by the following equation:

$$\tau = \frac{32\pi^3}{3} \cdot \frac{n_0^2}{N_0 \cdot \lambda^4} \cdot \frac{(C \cdot \delta \cdot n/\delta C)^2}{C \cdot \dfrac{\delta P/RT}{\delta C}} \qquad (1)$$

where τ is the turbidity of the solution in cm.$^{-1}$; n_0 is the refractive index of the solvent; N_0 is the Avogadro number; λ is the wave length in centimeters; C is the concentration in grams/ml.; $\delta n/\delta C$ is the concentration gradient of the refractive index; and $\dfrac{\delta P/RT}{\delta C}$ is the concentration gradient of the osmotic pressure.

The reciprocal dependence of turbidity on the concentration gradient of osmotic pressure expresses the basic Einstein relation between the amount of the fluctuations and the change of free energy during the creation of these fluctuations. The less the amount of the fluctuations, the greater should be the osmotic pressure which is able to bring about a local change in concentration.

Defining the constant quantities in Equation (1) by H, we get:

$$HC/\tau = \frac{\delta P/(RT)}{\delta C} \qquad (2)$$

where

$$H = \frac{32\pi^3}{3} \cdot \frac{n_0^2}{N_0 \cdot \lambda^4} \left(\frac{\delta N}{\delta C} \right)^2$$

* Translated for Rubber Chemistry and Technology from *Issledovaniya v Oblasti Vysokomolekulyarnykh Soedinenii, Doklady k 6-oi Konf. po Vysokomolekul. Soedineniyam*, 1949, pages 253–262.

The osmotic pressure of dilute solutions of high-polymer substances can be represented by the empirical equation:

$$P/(RT) = C/M + BC^2 + \ldots \quad (3)$$

where B is a constant which depends on the solvent-solute system, and M is the molecular weight of the dissolved substance.

Substituting and differentiating, we get:

$$HC/\tau = \frac{1}{M} + 2BC \quad (4)$$

Debye arrived at the very same result by means of a direct calculation of the particle field excited by the light falling on the particle. The calculation is possible in the region of very dilute solutions with small particles, which are considered as single dipoles vibrating with the wave length of the light. It is of considerable importance in the direct method for computing the intensity of the light-scattering to show that the final result is independent of the shape of the particle, since it is thus possible to ignore the particle shape in the calculation.

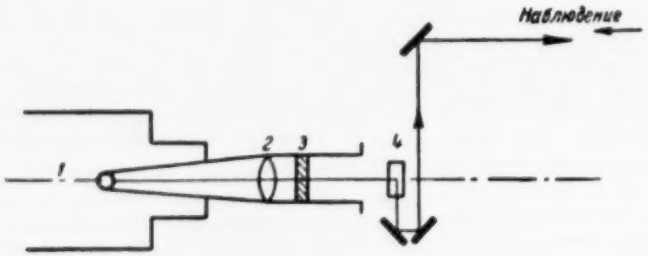

FIG. 1.—Diagram of the nephelometer. 1. Mercury lamp; 2. Lens; 3. Light filter; 4. Cell for the solution. The arrows at upper right indicate the point of observation.

In the expression for H, the concentration gradient of the refractive index $\delta n/\delta C$ may be replaced by the ratio $\frac{n - n_0}{C}$ where n is the refractive index of a solution of concentration C. Such a substitution is possible because of the fact that, in the regions of dilution usually studied, the difference $n - n_0$ is strictly proportional to concentration.

From Equation (4) it follows that the ratio HC/τ has a linear relation to concentration. The section of the ordinate intercepted by a straight line on the graph drawn in terms of $HC/\tau : C$ equals the reciprocal of the molecular weight. Hence, in order to determine the molecular weight according to the light-scattering, it is necessary to measure the refractive index of solvent and solution at any given concentration, as well as the intensity of the light-scattering for several concentrations. Also we determine graphically the limiting value of HC/τ where $C \rightarrow 0$; this being equal, as was shown above, to the reciprocal of the weight-average molecular weight value.

For refractive index measurements on solutions and solvents, we used the Pulfrich refractometer. The determination was made with the green line of the mercury lamp. The concentration gradient of the index of refraction was determined from measurements of the index of refraction of solutions of con-

centrations 0.8–1.2 g./100 ml. The light-scattering of the solution was measured with a Leitz nephelometer, with an angle of observation of 90°. The light source was the mercury lamp PRK-4, equipped with a light filter which transmitted only the green line in the mercury spectrum (λ = 546 mμ). For a turbidity standard, a cloudy glass rod was used, which was calibrated for absolute turbidity with a Zeiss prism of known turbidity.

Since the bulk of the solutions investigated had a considerably lower turbidity than the glass rod, intermediate standard solutions of gelatine in water were prepared. The accuracy of a turbidity measurement of an absolute value of 10^{-3} cm.$^{-1}$ amounted to 2.5 per cent. A diagram of the nephelometric apparatus is presented in Figure 1.

TABLE 1

Experiment No.	Substance	Solvent	Molecular weight: Light-scattering method	Molecular weight: Osmotic method	Molecular weight: Viscosity method
1	Polystyrene I (a heat-polymer)	Benzene	385,000	—	—
2	Polystyrene II (made with an initiator)	Benzene	200,000	—	—
3	Polymethyl methacrylate (fractionated)-I	Acetone	417,000	—	—
4	II	Acetone	588,000	—	—
5	III	Acetone	625,000	—	—
6	IV	Acetone	2,000,000	—	—
7	Butadiene-styrene rubber (sol fraction)	Toluene	200,000	96,000	—
8	Butadiene-styrene rubber (commercial)	Benzene	—	370,000	440,00
9	Natural rubber (smoked sheet)	Toluene* (5% methanol)	200,000–280,000	200,000–240,000	178,000–† 200,000
10	Natural rubber (pale crepe—medium fraction)	Toluene* (5% methanol)	215,000–270,000	220,000	200,000
11	Brominated rubber (pale crepe)	Chloroform	400,000	—	—

* In Experiments 9 and 10, methanol was added only for the light-scattering method.
† The two values for molecular weight in Experiments 9 and 10 are the extremes of values obtained with various solutions made from one original rubber preparation.

By means of light-scattering, the molecular weight was determined for four fractions of various samples of polymethylmethacrylate, unfractionated polystyrene, butadiene-styrene rubber, two forms of natural rubber, and brominated rubber.

The solvents were carefully dried, and were purified by repeated distillations. The solutions of high-polymer substances were purified by reprecipitation and by filtration through glass filters of medium porosity. Natural rubber and butadiene-styrene rubber were extracted in the cold with acetone before precipitation. All operations with natural rubber were carried out in an atmosphere of purified nitrogen. The nitrogen was purified of any traces of oxygen and moisture by passing it over copper placed on silica gel, at 300° C, and then through a system of drying agents (sulfuric acid, calcium chloride, and phosphorous pentoxide).

The results of the molecular-weight determinations are presented in Table 1. In Figures 2 and 3 are given graphs for the determination of $[HC/\tau]_{c\to 0}$ for various compounds.

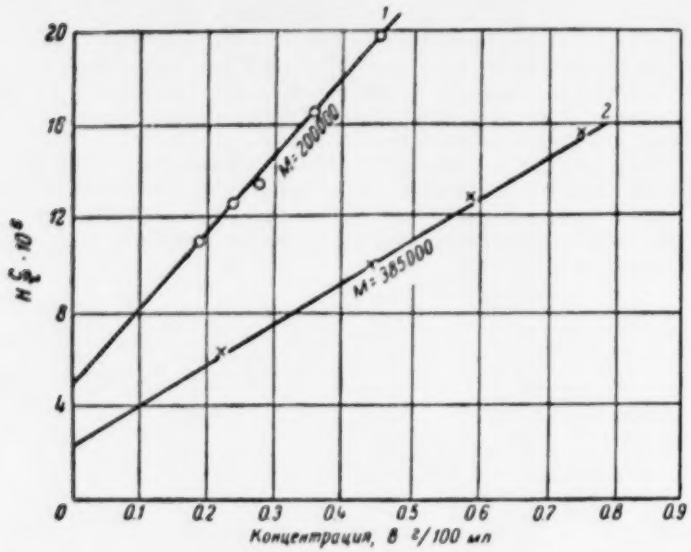

FIG. 2.—Determination of the molecular weight by light-scattering. 1. Butadiene-styrene rubber; 2. Polystyrene. The abscissa represents solution concentration in grams per 100 ml. *M* denotes molecular weight.

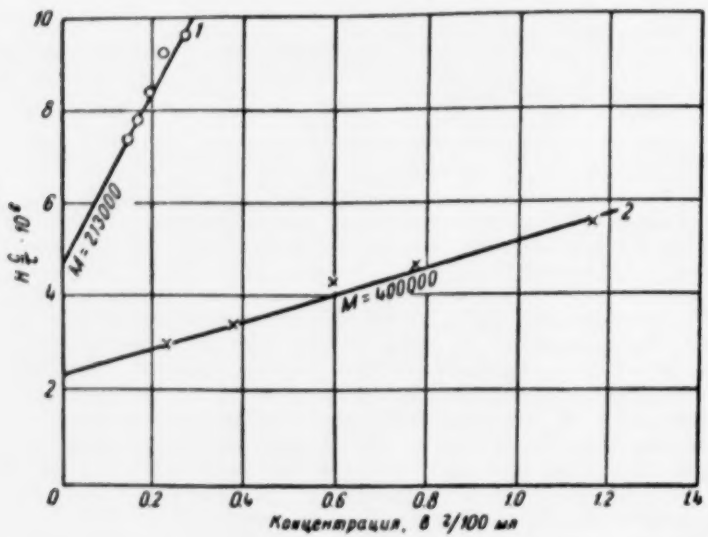

FIG. 3.—Determination of molecular weight by light-scattering. 1. Natural rubber; 2. Brominated natural rubber. The abscissa represents the concentration of the solution in grams per 100 ml. *M* denotes molecular weight.

THE OSMOTIC METHOD

For the osmotic measurement of molecular weight, we used the glass osmometer proposed by Dogadkin for measuring osmotic pressure by the static method, an apparatus whose use has become rather widespread within the last two years.

The osmometer (Figure 4) consists of a glass cell (*1*) with a capacity of about 15 ml. A semipermeable membrane serves as the bottom of the cell; this is attached to the ground glass flange of the cell (*2*). The solution is poured into the cell through the outlet tube (*3*), which is closed by means of the ground-glass stopper (*4*). An airtight closing is made possible by a mercury seal. The

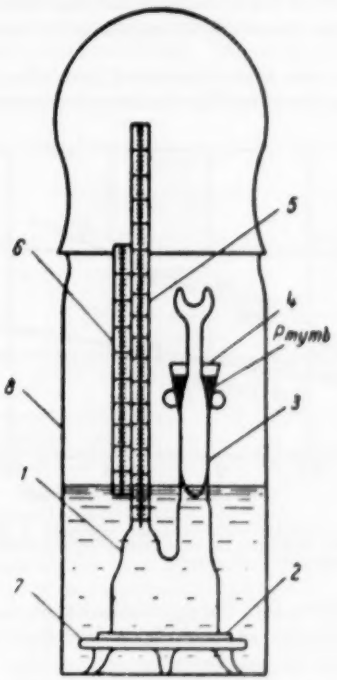

FIG. 4.—Diagram of the Dogadkin osmometer. The legend on the right-hand side of the diagram indicates mercury.

top part of the cell ends in a graduated capillary (*5*), with a diameter of 0.7 mm. and a length of 12–15 cm.; another capillary (*6*) exactly similar is attached to the first in such a way that its end is immersed in the solvent and serves for the calculation of capillarity. The cell is placed on the ground collar (*7*), which is set on the bottom of the vessel containing the solvent (*8*). The vessel is closed with a ground cover.

All of the work was done with membranes of the fine Ultracellafilter type; with these an equilibrium was reached within 4–6 hours after the start of the test. The membranes were treated with alcohol, and were cemented on with an aqueous solution of polyvinyl alcohol. These were then heated for 20 minutes at 70–100° C while the membrane was compressed gently. The cemented

membranes were then washed with the solvent, and after this the membranes were kept immersed in the solvent at all times until the start of the test[4].

Before the osmometer is filled the temperature of the solution and of the solvent are adjusted to 25° C. The solution is poured into the cell, and, by a movement of the stopper and a slight tilting of the cell, the solution is brought to any desired level. The excess solution is forced out, by the insertion of the stopper, to a point above the ground-glass portion. Mercury is poured on the stopper, and the excess solution above is removed with filter paper. The cell is placed carefully, so as not to damage the membrane, on the collar in the vessel, in which the solvent has already been placed. The level of the latter is made even with the lower level of the mercury in the side-tube.

The vessel containing the cell is immersed in a constant-temperature bath at 25 ± 0.1° C.

The amount of the rise h is determined from the difference between the levels of the control capillary and the capillary connected with the cell.

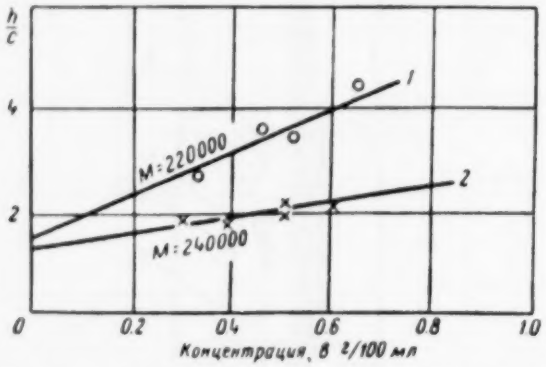

FIG. 5.—Determination of molecular weight by osmotic pressure. 1. Medium fraction of pale crepe. 2. Smoked sheet. The abscissa represents the concentration of the solution in grams per 100 ml.; the ordinate the ratio h/C. M denotes molecular weight.

At the beginning of the test the concentration of the solution in the cell is determined. The calculation of molecular weight from osmotic experiments is carried out according to the equation:

$$M = \frac{RT}{\delta} : \lim_{C \to 0} \frac{h}{C}$$

where the limiting value of h/C is determined by means of a graph (Figure 5).

DISCUSSION OF RESULTS

As has been noted, the light-scattering method gives the weight-average molecular weight, and is not affected by the shape of the particle being investigated. As a consequence of this, the light-scattering method in many cases proves to be uniquely suitable for research. An important virtue of the method, also, is the fact that it makes possible work with very dilute solutions, and that the higher the molecular weight, the lower can be the concentration of the solution being studied.

However, the method has its inherent limitations, as well as certain experimental difficulties. Among the former is, first of all, the limitation in the size of the particles being investigated. The necessity of introducing a correction for the presence of particles comparable in size to the wave length increases the possibility of error in the determination. In some isolated cases, for instance, with a natural rubber solution, it has proven possible to avoid the correction by the choice of the solvent. The configuration of molecules in solution depends on the solvent. Apparently in "good" solvents the bends in the high-polymer molecules are laid together more loosely and, as a consequence of this, have a greater volume. We should carefully take note of such circumstances, since the compression of the separate molecules in "bad" solvents is always accompanied by the formation of aggregates, and in some cases the aggregates survive even in highly dilute solutions. The latter situation may lead to a determination of the particle weight instead of the molecular weight, even under conditions of extrapolation to infinite dilution (as with natural rubber in halogenated solvents).

TABLE 2

Solution	Method of determining molecular weight	Molecular weight	Author
Natural rubber in toluene	Osmotic method	200,000–240,000	Present work
Natural rubber in ether (sol-rubber)	Ultracentrifuge method	400,000–435,000	Kraemer[5]
Natural rubber in carbon tetrachloride	Diffusion measurement method	400,000	Pasynskiĭ and Gatovskaya[6]
Natural rubber in toluene with 5% alcohol	Light-scattering method	200,000–280,000	Present work

Among the experimental difficulties of this method is the necessity for a sufficiently great difference between the refractive indexes of solution and solvent. On the basis of our determinations and the data of other research workers, it was established that the difference in refractive indexes for 1 per cent solutions should be about 0.0005–0.001.

Because of this, several commonly used solvents, such as benzene, toluene and gasoline, are unsuitable for natural rubber. Sometimes the difficulty may be overcome by the use of two-component mixed solvents, but this is undesirable, since it complicates the work of measurement considerably.

Among the experimental difficulties of this method, we may also take note of the prohibitively high requirements for the purity of the solutions to be tested. Lower molecular weight impurities, if present in only such quantities as not to change the index of refraction, are of no great importance. Mechanical contamination is easily avoided and thus causes no complication of the work. The greatest obstacle, however, is found in the high molecular-weight contaminants, since their removal is always difficult, and the presence of even insignificant quantities in the test solution may change the results of the determination completely. With colored solutions it is almost always possible to choose a primary color which is outside of their absorption range on the spectrum. However, the necessity of investigating a broad region of the spectrum in this case likewise involves difficulty.

The experimental difficulties noted are not insuperable, however, and the comparative simplicity of the design of the apparatus and the speed with which results are obtained have made a wide utilization of the method desirable in the performance of our research work.

In comparing the molecular weight values which we obtained by the method of light-scattering and by the osmotic method, we note that the results agree satisfactorily. In certain cases the values for light-scattering are higher than the osmotic data, which is perfectly natural for polydispersed systems, since light-scattering gives the weight-average molecular weight, while the osmotic method gives the mean weight.

The results obtained by us for the molecular weight of natural rubber, by both the light-scattering and the osmotic methods, agree with values found earlier (see Table 2). The discrepancies are not in excess of those usually found when different preparations are used.

CONCLUSIONS

1. An account is given of experiments to determine the molecular weight of natural rubber and other high molecular-weight compounds by light-scattering and osmometry.

2. A new design of osmometer for determining molecular weight is described.

3. It is shown that the light-scattering method gives molecular weight values which agree satisfactorily with those given by the osmotic method.

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[3] Einstein and Smoluchovskil, *Ann. Physik* **25**, 205 (1908).
[4] Recently we have used collodion membranes prepared according to Montonna and Jilk (*J. Phys. Chem.* **45**, 1376 (1941). The membrane is attached, not only to the flange of the cell, but also to the collar, which is clamped to the cell by a weight when the membrane is stuck onto the collar. Thus the membrane is held firmly, and the osmometer may be used with one membrane for several months of uninterrupted work.
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[6] Pasynskil and Gatovskaya, *Zhur. Fiz. Khim.* **20**, 715 (1946).

THE PLASTICIZATION OF BUTADIENE-STYRENE RUBBER *

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The process of plasticization produces in the structure of rubber, and therefore in its properties, a number of reversible and irreversible changes. The former include partial breakdown of the secondary formations; the latter, destruction of the chain molecules and a change in their forms. Under factory conditions of plasticization, on rubber mills or in closed plasticizing machines these changes result from mechanical, oxygen, and thermal action. Determining the influence of each of these factors separately presents considerable difficulty under these conditions. However, by carrying out the plasticization at low temperatures, we can reveal the role of the mechanical reactions, excluding the thermal ones, almost completely; while by conducting the plasticization at an elevated temperature in an atmosphere of an inert gas or in the presence of oxidation inhibitors, we may clearly delineate the effect of the thermal action itself.

The problem of a research worker in the field of the study of the plasticization process at present does not consist of seeking evidence of the existence of the numerous individual reactions; adequate evidence of this kind is found in the results of the work of Dogadkin[1], Novikov[2], Farberov, Suslyakov, and Margolina[3], Staudinger[4], Busse[5], etc. The problem consists, instead, of a more intensive examination of the structural changes brought about in rubber by these partial reactions, a study of their effects on the technological and commercial properties of rubber and its vulcanizates, and a selection of the most efficient and economical conditions for industrial plasticization, which is not at all ideal at the present time. Before going into a study of the plasticization process on this plane, however, we must choose in a practical way conditions which permit us to produce plasticized rubbers differing considerably from one another in their properties.

It is necessary to separate the structurizing reactions from the destructive reactions, since the preservation of a linear structure in the molecule is, from our point of view, of considerable importance in the structure of the plasticized product. The occurrence of a branched three-dimensional structure as a result of a linking of the molecules (at the time of their destruction) should cause a deterioration of the commercial properties of rubber stocks and of vulcanizates of these. As will be seen later, this proposition has been fully confirmed by experiment. The study of plasticization kinetics presents a means of choosing the conditions that we need for the purposes noted above. The point is that, by tracing the change of the kinetics of rubber plasticization through a change of the plastic properties, we can detect at once whether both reactions (structure formation and destruction) are going on simultaneously or whether one or the other is proceeding alone. In the first case, the kinetic curves show one property

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or another of the rubber as passing through a maximum or minimum; in the second case the kinetic curves obtained show the steady rise or fall of some property.

Figure 1 shows a set of experiments in plasticization on a rubber mill at 20–30° C. It is evident from the diagram that even fairly prolonged treatment (up to 300 minutes) does not cause any decrease of plasticity. Such a result indicates that no structure forming reactions are to be found in this case, and that the number of three-dimensional branchings of molecules does not increase under these conditions.

The kinetics of plasticization at temperatures below 30° is described adequately by the equation:

$$P = P_0 + a(1 - e^{-k_1\tau}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

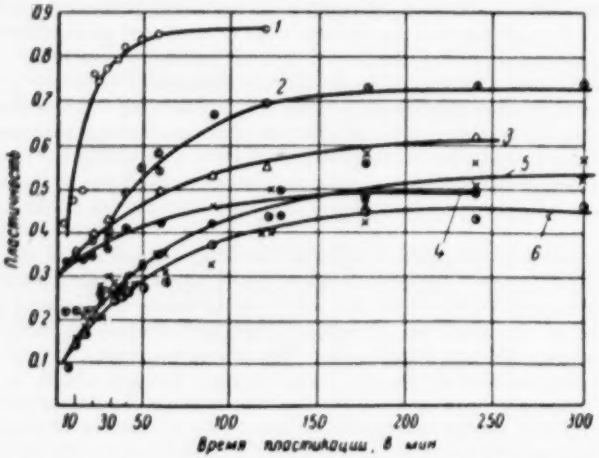

FIG. 1.—The kinetics of plasticization of rubbers on a laboratory mill with the rubber at temperatures of 20–30° C. 1—Smoked sheet; 2—Buna-88; 3—Soft butadiene-styrene polymer; 4—JR8 rubber; 5-Buna-8-3; 6—Buna-N. The abscissa represents the plasticization time in minutes; the ordinate represents plasticity.

where P is the plasticity of the rubber at the moment of time (τ); P_0 is the original plasticity of the rubber; k_1 is the constant of plasticization rate; a is the proportionality constant between the number of acts of destruction and the plasticity. The applicability of this equation is confirmed by the way in which the experimental points fall on the theoretical curves for various kinds of rubbers (Figure 1).

If plasticization at low temperatures is not accompanied by structure formation, the plasticization of butadiene-styrene copolymers at elevated temperatures (the so-called thermo-oxidative plasticization) is related to the simultaneous operation of destruction and structure forming reactions. In kinetic data this appears as a maximum on the plasticity curve. Figure 2 presents results of plasticization in a laboratory banbury machine at a temperature of 140–145° C. The aforementioned phenomenon has been noted repeatedly, but the interpretation of it has been faulty. It was supposed that the process of structure formation began after the destruction process was essentially finished. How

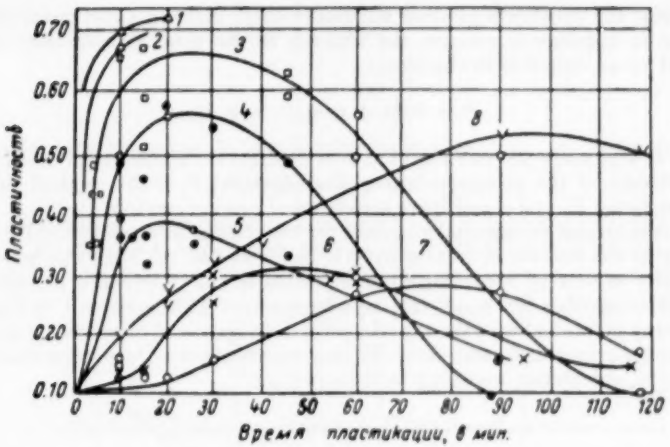

FIG. 2.—The kinetics of plasticization of Buna-S-3 rubber in a laboratory banbury at 140° C, with various proportions of plasticizer. 1.—With 5 parts by wt. of plasticizer on 100 parts by wt. of rubber; 2.—4 parts; 3—3. parts; 4.—2.5 parts; 5.—2.0 parts; 6.—1.5 parts; 7.—1 part; 8.—Without plasticizer.

widespread such an opinion is can be seen even in the form of the equation used in some German work to describe the softening of Buna S-3 in a boiler, as follows:

$$D = D_0 \cdot e^{-k\tau\alpha} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

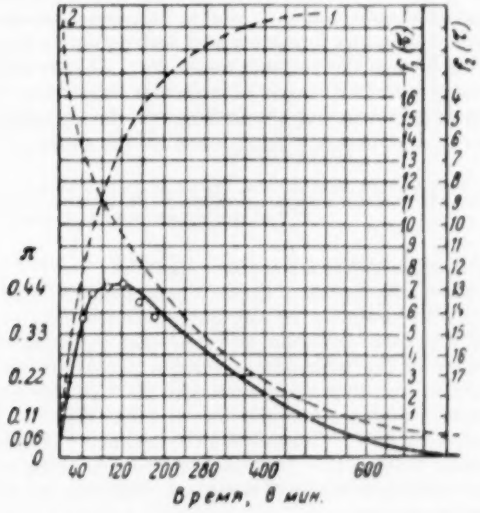

FIG. 3.—Comparison of the experimental kinetic curves of plasticization of Buna-S-3 rubber without a plasticizer in a laboratory banbury at 140° C, with the theoretical kinetic curve obtained from Equation (3). The abscissa represents the time of plasticization in minutes; the ordinate scale on the left represents plasticity, while those on the right represent the values of the functions $f_1(\tau)$ and $f_2(\tau)$ as expressed in broken curves *1* and *2*, respectively. The solid curve represents the experimental data.

When the reactions proceed simultaneously, causing these properties to change in opposite directions, the kinetics of the total process may be described by an equation in the form:

$$P = P_0(1 + a \cdot m)(1 - b \cdot n) \quad (3)$$

where m and n are the number of acts of destruction and structure formation, respectively, of the polymers during plasticization; P_0 is the original value of the plasticity P; and a and b are constants of proportionality.

A comparison of experimental data for the change in plasticity of Buna S-3 rubber in the process of treatment in a boiler at 140° C, with the indexes of plasticity calculated according to an equation of the proposed type, indicates that this describes hot plasticization adequately. This is evident in Figure 3 where the points indicate the experimental data (series of experiments done at atmospheric pressure), and the solid line represents the theoretical change of plasticity, calculated according to the equation:

$$P = 0.003[1 + f_1(\tau)][1 - f_2(\tau)] \quad (4)$$

The course of the functions $x = f_1(\tau)$ and $y = f_2(\tau)$ is delineated in Figure 3 by the rising and falling broken curves, respectively. Figure 3 demonstrates that the most rapid process of structure formation can be combined at the same time with a rapid increase of plasticity; and this is true not only when the plasticity is passing through a maximum. According to this, three-dimensional branched molecules should emerge at the very beginning of the process; this is revealed in the properties of polymers which have been even slightly plasticized by the hot method.

In order to describe the structural change of polymers in the plasticization process and to relate these changes to plastic properties, let us examine separately the influence of structure formation and destruction on the average molecular weight and the form of the polymer molecules. It is evident that each act of destruction brings about a decrease of molecular weight and that the average molecular weight $\bar{M}_m$, in a period of plasticization during which the one chain undergoes m acts of destruction is determined by the equation:

$$\bar{M}_m = \frac{\bar{M}_0}{1 + m} \quad (5)$$

where $\bar{M}_0$ is the average initial molecular weight.

During this, the configuration of the molecules should not change, assuming that scission is equally probable for any bond between links of the chain.

In the case of structure formation, however, each act brings with it a change in the configuration of the molecules, since the probability of two molecules being linked together end-to-end is practically nil. In this system there is a gradual accumulation of new structural forms, which may be characterized by the degree of branching (W). Considering the branching in a linear polymer as unity, and assuming that, in the plasticization process during a given period of time, the polymer undergoes n acts of structure formation, we may characterize this in the following manner:

$$W = 1 + \frac{n}{N_m} \quad (6)$$

where N_m is the number of linear fragments of molecules within the system at a given moment; this is evidently equal to:

$$N_m = N_0 \cdot \frac{\bar{M}_0}{\bar{M}_m} \quad \ldots\ldots (7)$$

Transforming Equation (3) into the following form:

$$P = (a_1 + b_1 m)(a_2 - b_2 n)$$

and substituting in this the values of m and n from Equations (5) and (6), we obtain an approximate equation for plasticity which depends on the average molecular weight and the degree of branching:

$$P = \left[\frac{b_1 \bar{M}_0 - (b_1 - a_1)\bar{M}_m}{\bar{M}_m} \right] \left[\frac{(b_2 - b_2 W)\bar{M}_0 + a_2 \bar{M}_m}{\bar{M}_m} \right] \quad \ldots\ldots (8)$$

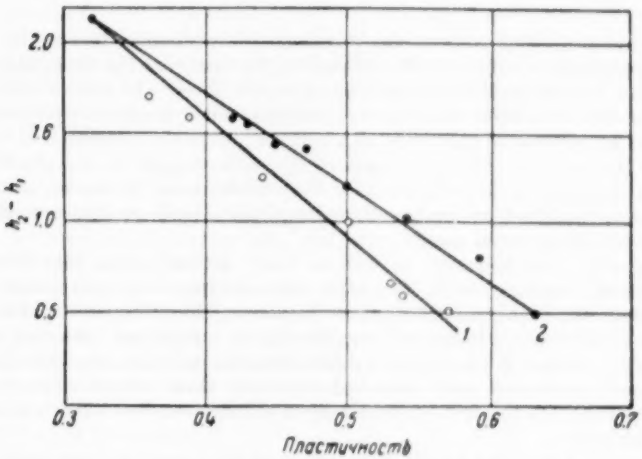

FIG. 4.—Dependence of recovery capacity on plasticity in the plasticization of a soft polymer on a cold mill (*1*) and in a boiler at 140° C (*2*). The abscissa represents plasticity; the ordinate the recovery figure of samples in a Williams plastometer (see Reference 6).

With a decrease of molecular weight, the interaction between molecules decreases, and by the action of the same internal force, the polymer is distorted appreciably. With the formation of branched molecules, consisting of linear fragments from the scission of molecular chains linked together, the polymer's capacity for elastic recovery rises. Here the same thing happens as in vulcanization, where intermolecular bridges introduce a mutual distortion of the chains and permit the material to recover its shape rapidly after the load is removed. Thus a change in the capacity for recovery[6] may characterize changes in the extent of branching of a polymer in the plasticization process. And in fact, as can be seen in Figure 4, plasticized material obtained from cold processing has a lower recovery capacity $(h_2 - h_1)$, for the same plasticity, than plasticized material obtained from hot processing.

The breakdown of the three-dimensional structures under cold plasticization, or at any rate the absence of newly formed three-dimensional molecules,

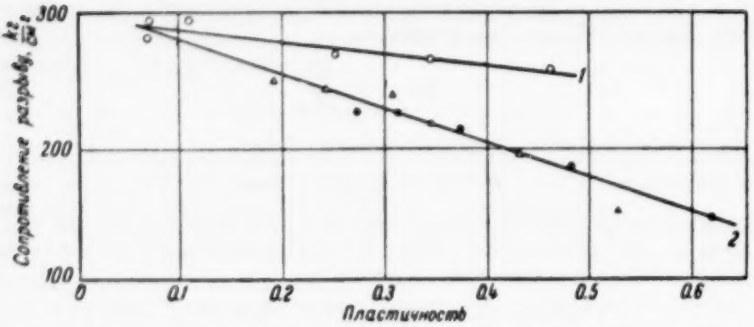

FIG. 5.—Dependence of tensile strength of vulcanizates on the plasticity of the stiff polymer when plasticized on a cold mill (*1*) and in a banbury at 145° or a boiler at 140° C (*2*). The abscissa represents plasticity; the ordinate tensile strength in kg. per sq. cm.

should show up favorably in the physical and mechanical properties of vulcanizates of these rubbers. Plasticization, by reducing the molecular weight of rubber, usually impairs the quality of pure rubbers. In rubber with carbon black or other additives, this effect of plasticization is somewhat reduced, inasmuch as an increase of plasticity, as a rule, improves the dispersion of the additive in the rubber. If the decrease of molecular weight in the plasticization process, however, is accompanied by the simultaneous formation of three-dimensional branched molecules, then its physical and mechanical properties should deteriorate even more.

Dogadkin and Karmin[7], as well as Gee[8], demonstrated that the tensile strength of vulcanizates at optimum vulcanization is proportionate to the amount of the highly oriented phase present. Doubtless the orientation of branched molecules is hampered considerably in comparison with that of linear molecules. Thus, if plasticized rubber obtained by thermal-oxidative treatment really contains more branched molecules than cold-plasticized rubber, stocks made from the former should have a lower tensile strength than those from the latter.

Figure 5 shows that tensile strengths of stocks from hot-plasticized rubbers

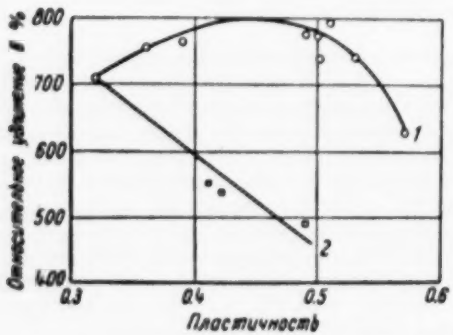

FIG. 6.—The relation of the percentage elongation of a vulcanizate to the plasticity of the soft polymer when plasticized on a cold mill (*1*) and in a banbury at 145° C (*2*). The abscissa represents the plasticity; the ordinate the percentage elongation.

are lower in all cases than those of stocks from cold-plasticized rubbers. A comparison of Figures 4 and 5 shows that the tensile strengths of vulcanizates are closely related to the structural parameters of plasticized rubbers: their molecular weight (a decrease of which shows up as increased plasticity) and degree of molecular branching (an increase of which is reflected in an increase in capacity for recovery). It follows from Figure 6 that vulcanizates from cold-plasticized rubber give stocks with a high percentage elongation, which is likewise explained by its lower content of branched three-dimensional molecules which would hinder the elongation of the stock.

CONCLUSIONS

1. The kinetics of the plasticization of a butadiene-styrene copolymer on a cold laboratory mill was studied. It was established that, at temperatures of 20–30° C, the plasticity rises steadily and that, consequently, under these conditions a monodirectional destructive process takes place.

2. The kinetics of plasticization of a butadiene-styrene copolymer was investigated in a laboratory banbury at 140° C, both with and without a plasticization aid (chemical). Plasticization at a high temperature is accompanied by the simultaneous operation of the two reactions of destruction and structure formation proceeding at cross-purposes, and may be described by a kinetic equation of the type:

$$P = P_0(1 + a \cdot m)(1 - b \cdot n)$$

3. Plasticized rubbers obtained by breakdown on a cold mill have a smaller capacity for recovery than those obtained by treatment in a boiler or a banbury at temperatures above 120° C.

4. Plasticized rubbers obtained by milling on a cold mill give stocks with higher tensile strength and higher relative elongation than rubbers plasticized by hot treatment.

5. The high recovery capacity of rubbers plasticized at elevated temperatures and the lowering of the physical and mechanical properties of vulcanizates of those rubbers are explained by the branched molecules which they form during structure formation.

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GLASS TRANSITIONS IN POLYMER-PLASTICIZER SYSTEMS *

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An elastomer, on cooling, is transformed within a fairly narrow temperature range from a relatively elastic, readily processed material to a hard brittle glass-like mass. The "glass transition" region of a polymeric system serves to define a temperature below which rubberlike properties cannot exist. Transition phenomena in polymers are discussed by Boyer[1] in a review, with an extensive bibliography to 1952.

In this study it was desired to ascertain, in broad outline, the properties of a diluent which promote flexibility in elastomeric blends by postponing the glass transition to lower temperatures.

EXPERIMENTAL

Of the properties which may be measured to determine a glass temperature, relative volume was selected for its simplicity and convenience. The dilatometer designed by Bekkedahl and Wood[2] was used for pure polymers and their blends with diluents. A glass bead at the neck of the bulb prevented clogging of the capillary by polymer and a glass plug served to avoid degradation of the polymer and ignition of diluent when the bulb was sealed off. A silicone oil[3] was chosen as confining fluid because of its low swelling power and its linear V-T relation to at least —100° C. With but two exceptions noted elsewhere in this paper, the miscibilities of the silicone oil with the diluents were low enough to preclude appreciable extraction of the latter from blends with polymer.

Filling of the dilatometer with the silicone oil was accomplished by small increments under vacuum, except when the diluent was too volatile. With care, most air pockets could be eliminated by alternate cooling and gentle warming. The presence of some air was tolerable; it was unnecessary to calculate specific volumes since the determination of a glass temperature could be made from direct dilatometer readings. A U-type dilatometer was used for measurements on liquids less dense than the confining fluid. Temperature control was achieved by immersing the dilatometer in a well stirred Dewar flask containing methanol, cooled by the addition of dry ice or liquid nitrogen as required. Temperatures were determined with a platinum resistance thermometer in a bridge circuit with a sensitive galvanometer as detector. The height of the liquid level could be estimated to within 0.2 mm. on a scale fixed to the capillary of the dilatometer. Unless otherwise specified, ten to fifteen minutes were allowed to elapse at each temperature before a volume reading was made. The precision of the T_g determinations is estimated as $\pm 1°$ C.

Several measurements of low-temperature flexibility were also made, using a modified Gehman test[5]. A vulcanized polymer containing the plasticizer

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TABLE I

ESTER PLASTICIZERS IN GR-S

Diluent	Vol. increase on swelling of vulcanizate %	Max ΔT_g ° C	$(\delta_{GR-S} - \delta_{dil})^{2}$ [a,b]
Methylphthalyl-ethyl glycollate[c]	1.5	2	3.8
Dicarbitol phthalate[d]	1.6	2.5	4.5
Tributoxyethyl phosphate[d]	17.7	16	0.1
Dibutyl phthalate[e]	33.1	24	0.7
Dioctyl adipate[d]	50.0	37	0.0
Dioctyl sebacate[f]	51.7	38	0.0
Dibutyl sebacate[f]	55.2	9	0.0

[a] δ_{GR-S} taken as 8.6.
[b] δ_{dil} (diluent) calculated from molar attraction constants[4].
[c] Monsanto Chemical Co.
[d] Ohio Apex, Inc.
[e] Carbide and Carbon Chemical Co.
[f] Resinous Products and Chemicals Co.

and 50 parts Philblack-O per hundred of blend was subjected to torsional stress by means of a suspended wire clamped to its end; the angular response was measured after ten seconds.

The source and purity of the diluents are recorded in Tables I, II, III, and IV. These materials were used as received. Blends were prepared by the addition of diluent to polymer on a cold mill to facilitate rapid dispersion. Mixtures containing in excess of 15 parts of diluent with a melting point higher than 130° C (Tables II, III, and IV) were generally not homogeneous. After some time, separation of solid was evident at about 25° C. The remaining blends appeared to be true solutions at room temperature. The polymers were

TABLE II

HIGH-MELTING COMPOUNDS IN BUTYL RUBBER

Diluent	Melting point (° C)	Loading wt. diluent per hundred polymer	Glass temperature (° C)
—	—	nil	−74.0
Adipic acid[a]	151	10	−75.8
Sebacic acid[b]	153	50	−72.0
Succinic acid[c]	185	30	−73.0
n-Octadecanol[c]	59	20	−74.5
n-Decanol[c]	−6	30	−73.0
Ethyleneglycol[d]	−17	10	−75.5
Mannitol[a]	166	30	−72.0
Stearic acid[a]	69.4	10	−73.3
Capric acid[a]	31.5	10	−73.0
		50	−72.0
Dibutyl sebacate	−20	14	−73.5
		39	−74.0
n-Octanol[c]	−16	10	−77.5
		30	−79.5
Valeric acid[d]	−34.5	10	−78.0
		30	−84.0

[a] Reagent grade, Matheson Company, Inc.
[b] Practical grade, Matheson Company, Inc.
[c] Reagent grade, Eastman Kodak Company.
[d] "Purified," Central Scientific Company, Toronto.
[e] National Bureau of Standards.

TABLE III

HIGH-MELTING COMPOUNDS IN NITRILE RUBBER

Diluent	Melting point (° C)	Loading wt. diluent per hundred polymer	Glass temperature (° C)
—	—	nil	−32.5
Sebacic acid	133	5	−33
Succinic acid	185	30	−29.3
Mannitol	166	30	−32.5
Stearic acid	69	10	−32.5
n-Octadecane	27	5	−28.5
Valeric acid	−34.5	10	−41.3
		30	−52.5
Hexachlorobutadiene[a]	−22	42	−41

[a] Hooker Electrochemical Co.

Polymer Corporation Limited production samples. GR-S was a high molecular weight butadiene-styrene copolymer obtained at 72 per cent conversion from a 72/28 butadiene/styrene charge ratio at 5° C. The composition of the nitrile and Butyl rubbers were 68/32 butadiene-acrylonitrile and 98/2 isobutylene-isoprene, respectively. All dilatometric glass temperatures reported here refer to unfilled, uncured polymers and blends.

RESULTS AND DISCUSSION

For our purposes the diluents can be conveniently classed as diester plasticizers, crystalline solids, and hydrocarbon oils.

ESTER PLASTICIZERS

Figure 1 presents experiments volume-temperature data for a typical compatible system, dioctyl phthalate-GR-S. The curves consist of the usual two linear segments intersecting at T_g. Larger scale plots sometimes revealed a curved transition region; the extrapolations to a point of intersection then gave the characteristic temperature.

The effect of plasticizer concentration in two typical GR-S compatible systems is illustrated by Figure 2. The lower curve for dibutyl phthalate shows

TABLE IV

HIGH-MELTING COMPOUNDS IN GR-S

Diluent	Melting point (° C)	Loading wt. diluent per hundred polymer	Glass temperature (° C)
—	—	nil	−62.5
Adipic acid	151–3	15	−61.0
Succinic acid	133	5	−61.0
n-Octadecanol	59	50	−61.5
n-Octanol	−16.3	30	−62.5
Ethyleneglycol	−12	10	−60.0
Mannitol	166	30	−63.5
Stearic acid	69.4	30	−60.0
Capric acid	31.5	30	−62.5
Valeric acid	−34.5	30	−75.5
		10	−67.5

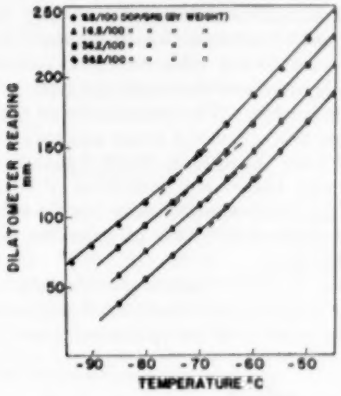

FIG. 1.—Dioctyl phthalate in GR-S.

the limiting or "saturation" effect of high plasticizer concentrations. This behavior was evident in every system investigated at sufficiently high diluent loadings. The saturation effect in dioctyl phthalate-GR-S blends would presumably be evident at higher plasticizer concentrations. The deviation of the glass temperatures at zero plasticizer concentration is probably a reflection of differences in nonpolymer content, mostly soap, between two production samples of the copolymer.

Additional data for a series of ester blends, including certain literature values[6], were analyzed. The properties of interest for each system were: the maximum depression of the glass temperature, the concentration of diluent at which a saturation effect is evident, and the compatibility of the two components. The data in Table I illustrate the relationship between compatibility and the maximum effect on the glass temperature. The second column gives the maximum experimental volume increase of a standard vulcanizate swollen at 55° C in an excess of each ester. According to the Flory-Rehner theory[7] of swelling of polymer networks, the magnitude of the volume increase for a fixed degree of cross linking—assured by the use of a standard vulcanizate—is a

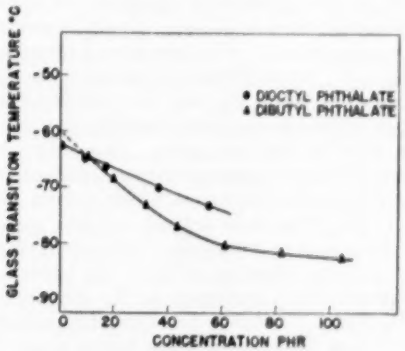

FIG. 2.—Typical GR-S compatible systems.

measure of solvent-polymer interaction. Specifically, the interaction parameter is related to the heat of solution, which, at least in the simplest cases, is proportional to the square of the difference between the so-called solubility parameters, δ, for the polymer and the swelling agent. The best solvent is one for which this difference is least. The parameters of the esters were calculated from their structures and the scheme of molar attraction constants proposed by Small[4]. It is observed from the data in Table I that there is rough agreement between experimental and theoretical estimates of compatibility on the one hand, and between $\Delta T_{g_{max}}$ and compatibility on the other. Dibutyl sebacate does not fit the pattern established by the other esters, and will be considered in another section of this paper.

The curves of Figure 3 show a linear relationship between the maximum depression of the glass temperature of uncured polymers and (1) volume increase on swelling of the corresponding vulcanizate and (2) the ester concentra-

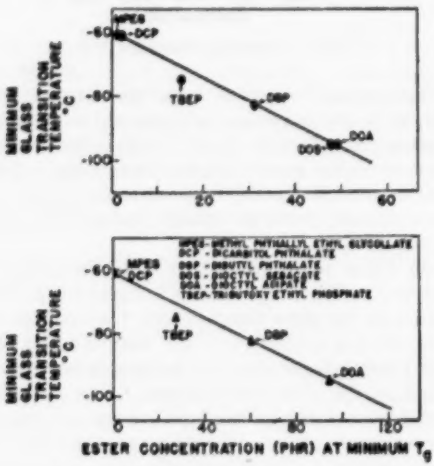

FIG. 3.—Effect of ester plasticizers on GR-S.

tion beyond which T_g is not appreciably changed. It appears, therefore, that the saturation effect at high ester loadings is closely related to the compatibility of the components of the blend. Whether actual phase separation of excess diluent, or "sweating out", occurs at the saturation concentration is not known. The glassy state (i.e., at or below T_g) may be considered[8] as one in which the rate of relative motion of the kinetic units has fallen to a value of the same order of magnitude as the experimental time-scale. In a pure polymer the segmental jump rate and its temperature dependence are determined by structural details, intermolecular, and intramolecular forces which govern local frictional resistance. The effect of plasticizer is to replace polymer segment—segment contacts by plasticizer—segment associations to an extent dictated by the plasticizer concentration and its solvating ability. If phase separation does not occur, saturation presumably corresponds to the plasticizer concentration beyond which local frictional resistance to segmental mobility is not materially diminished. Jenckel[9] has determined glass temperature by refractive index measurements on several polystyrene-plasticizer blends over very wide con-

centration ranges. His results indicate if the that plasticizer has sufficient solvent ability to ensure complete miscibility in all proportions with polymer, and if the plasticizer itself undergoes a glass transition, then T_g for the blends can vary continuously between the glass temperatures of the pure components. In such systems the glass temperature of the pure diluent appears to be the significant property.

CRYSTALLINE SOLIDS

Volume-temperature measurements were made on blends of GR-S, nitrile, and Butyl rubbers with a variety of compounds including carboxylic acids, alcohols, and hydrocarbons. Typical results are shown in Tables II, III, and IV. With the exceptions of dibutyl sebacate, valeric acid, and hexachlorobutadiene, the diluents were high melting solids which crystallized readily and effected virtually no depression of the glass temperature in blends. Evidence for crystallization in octadecane-GR-S blends is provided by the nature of the

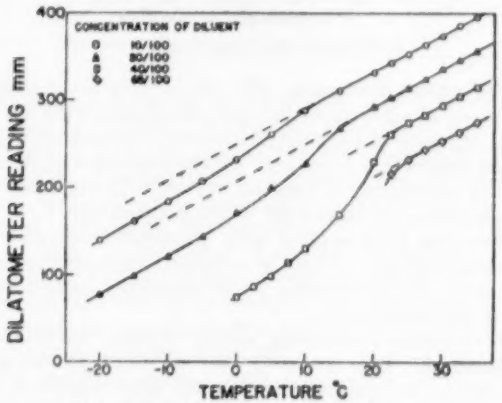

FIG. 4.—Crystallization of octadecane in GR-S.

volume-temperature curves of Figure 4. Similar curves were obtained for Butyl rubber diluted with varying amounts of dibutyl sebacate. The glass transition temperatures of these blends are the same as for pure polymer, completely independent of the diluent concentration (see Figure 5). Failure to depress the glass temperature is attributed to the crystallization of the diluent: at sufficiently low temperatures, though still above T_g, the blends are two-phase systems composed of essentially pure polymer and pure cyrstalline diluent. Even a fairly high melting diluent, however, may exhibit low temperature plasticizing ability if it is prone to supercool.

The plasticizing ability for GR-S of dibutyl sebacate, which crystallizes readily from its blends with polymers[10] is, on the other hand, attributed to the depression of the freezing point by polymer. This effect is qualitatively evident in Figure 4: the higher the polymer concentration, the lower the initial crystallization temperature. The system polymer-diluent is complete analogous to binary solutions of small molecules, and can be treated by the thermodynamics appropriate to polymer solutions[11]. It can be shown[12] that

$$\Delta\bar{F}_1 = 0 \simeq RT[\ln (1 - v_2) + v_2 + \chi v_2^2 + \Delta H_f \Delta T/T_f RT] \quad (1)$$

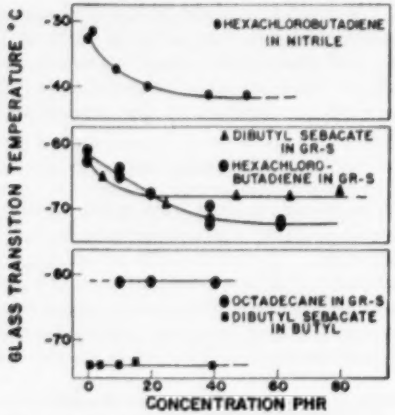

FIG. 5.—Effect of crystallizing diluents in polymers.

relates the freezing point depression, $\Delta T = T_f - T$, of crystalline diluent to the volume fraction, v_2, of amorphous polymer in solution with the liquid diluent. ΔH_f is the heat of fusion of the solid at its normal (absolute) freezing temperature T_f, χ is the interaction parameter for the polymer-liquid pair, and $\Delta \bar{F}_1$ is the partial molar free energy of transfer of liquid diluent from the solution of composition v_2 to the crystalline solid at the temperature T.

This equation has been applied with quantitative success to the system azobenzene-natural rubber. There is excellent agreement between the composition dependence of the freezing point calculated from Equation (1) and that reported in the literature[12].

The low-temperature plasticizing ability of some normally solid diluents can now be explained. It is necessary that sufficient diluent, as predicted by Equation (1), be in the liquid state below the glass transition temperature of pure polymer. This condition is apparently fulfilled by the polymer-diluent pairs shown in the upper curves of Figure 5, but not by the other two blends. The leveling off of the T_g vs. diluent concentration curves is attained at a temperature below which, regardless of the amount of diluent added, separation of excess solid leaves insufficient liquid to further depress T_g.

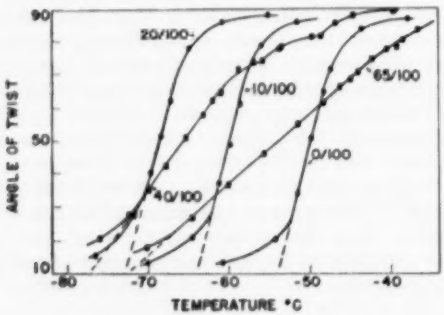

FIG. 6.—Dibutyl sebacate in GR-S.

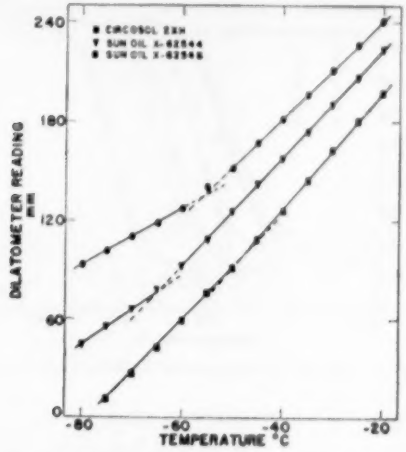

FIG. 7.—Glass transitions in oils.

Results which may be similarly interpreted have been obtained from Gehman tests on blends of GR-S with varying amounts of dibutyl sebacate. In Figure 6 it is seen that ten and twenty parts of the ester per hundred polymer shift the sigmoidal curves and the extrapolated freeze points by about ten and twenty degrees, respectively. At higher loadings there is no improvement in low-temperature properties. Furthermore, the sigmoidal curves have become distorted in a manner characteristic of crystallizing systems. The arcs on one of these curves (4.0/100) reflect the time-dependence of the crystallization. A smoother plot was obtained for the sample containing 65 parts of the ester when a standardized thermal treatment was adopted: after each measurement, the test sample was brought to room temperature and permitted to relax for fifteen minutes. The ineffectiveness of high dibutyl sebacate concentrations, i.e., greater than about 20 parts per hundred, can again be attributed to the separation of excess solid at the low temperatures of these experiments.

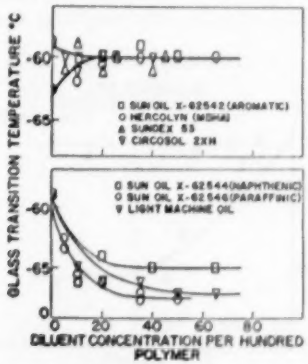

FIG. 8.—Blends of commercial oils with GR-S.

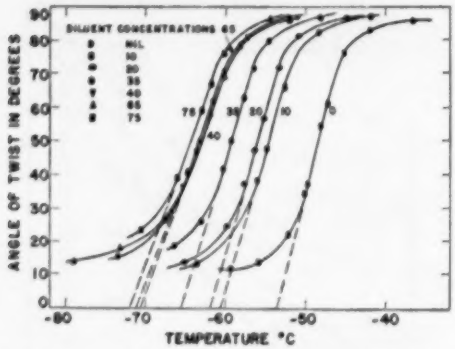

Fig. 9.—Gehman curves for sun oil X-62546/GR-S blends.

HYDROCARBON OILS

Several hydrocarbons, some of which were obtained from crude oil as cuts in the processing oil range, were investigated with the U-type dilatometer. The data, some of which are plotted in Figure 7, reveal breaks in the volume-temperature curve just as for polymers in the glass transition region. The linear segment of the high temperature range corresponds to the normal volume contraction on cooling of the liquid. At lower temperatures the volume decrease corresponds to the normal contraction of the oil in the glassy state. The change in slope of the volume-temperature curve for Sun Oil X-62546 at about —48° C is smaller than the corresponding changes for the other oils. Thus, though the volume data could be reproduced at will in successive cooling experiments, there is some uncertainty in this T_g assignment. The dilatometer readings for two oils, Sundex-53 and Sun Oil X-62542, were markedly time-dependent at temperatures, some ten to twenty degrees above T_g. Constant readings were obtained within about fifteen minutes at all other temperatures, even below T_g. The glass temperatures were readily located by extrapolation of accurately linear segments of the volume-temperature curves to points of intersection.

Heating experiments were also conducted, starting at the lowest temperature attained in the cooling cycle. On warming the sample about twenty

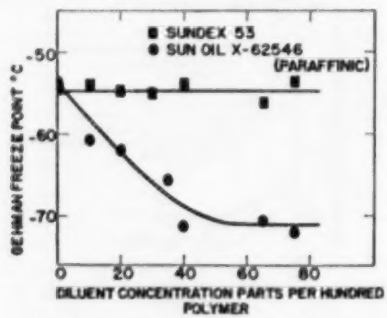

Fig. 10.—Freeze resistance of GR-S blends.

TABLE V

PHYSICAL PROPERTIES OF OILS: CORRELATION WITH ΔT_g OF GR-S BLENDS

Oil	T_g of oil (° C)	Pour point (° F)	Vol. increase on swelling GR-S (%)	Viscosity (Saybolt sec.) 100° F	Viscosity (Saybolt sec.) 210° F	Δ(log viscosity)[a] Δ(1/T)	Max. ΔT_g (° C)
X-62542[b]	−27.5	55	29.7	14500	178	3.63×10^3	1
Hercolyn[c]	−37	30	48.1	3930	90.9	3.16	−2.5
Sundex 53[b]	−27.5	51	90.6	2715	87.0	2.90	−2.5
Circosol 2XH[b]	−56	20	77.2	1815	90.4	2.53	−2.5
X-62544[b]	−65	0	58.2	1260	78.5	2.38	6
Light machine oil[d]	−40[f]	−8	90.6	271.5	55.7	1.64	8
X-6246[b]	−48[f]	+5	81.7	213.2	53.1	1.63	8.5
Diesel fuel[d]	< −60	+5	215	3.90[g]	1.39[g]	0.85	>25[j]
Iosol 2232[e]	< −90	—	265	0.695[g]	0.950[g,h]	0.69[i]	>30[j]

[a] From kinematic viscosities at 100° and 210° F.
[b] Sun Oil Co.
[c] Hercules Powder Co.
[d] Imperial Oil Ltd., Sarnia.
[e] Imperial Oil Ltd., Toronto.
[f] Uncertain.
[g] Viscosity in centistokes.
[h] Viscosity at 68° F.
[i] From kinematic viscosities at 68° and 100° F.
[j] The diluents were extracted by the confining fluid; these values are, therefore, lower limits.

degrees, conchoidal fractures, characteristic of glasses, developed and were accompanied by audible clicks. After cooling to the initial temperature, a higher dilatometer reading was obtained because of the voids formed on fracture. These phenomena strongly suggest that the oils are obtained in a glassy state at low temperatures.

Figure 8 shows the effect of concentration of these oil type diluents[14] on the dilatometric T_g of GR-S blends. Compounds shown in the upper section of this figure have virtually no plasticizing ability at low temperatures; the other oils can postpone the transition by 5 to 9 degrees.

Flexibility tests gave results completely analogous to those obtained by dilatometry. Figure 9 illustrates the plasticizing action of Sun Oil X-62546 at various loadings in GR-S. Extrapolation of the linear portions of the angular twist-temperature curves to zero twist gave the so-called Gehman freeze point. Figure 10, in which freeze points are plotted against oil concentration, may be compared with the corresponding dilatometric T_g vs. concentration curves shown in Figure 8.

An attempt was made to correlate low-temperature behavior of GR-S blends with some physical properties of the hydrocarbon oils. Diluents, ranging in consistency from a heavy processing oil, X-62542, to a light solvent, Iosol 2232, are arranged in Table V in order of increasing low-temperature plasticizing ability. There appears to be a trend toward greater plasticizing ability with decreasing glass temperature and decreasing pour point of the pure diluent, and also with increasing compatibility of the oil-polymer pair, as measured by the volume increase on swelling of vulcanizates. The most consistent correlation, however, exists between the data in the three columns on the right in Table V: the viscosity and its temperature coefficient on the one hand and the maximum depression of the glass temperature on the other. The relationship suggests a mechanical interpretation of plasticizing action. Effective diluents are those providing environments which are less resistant to the motion of polymeric segments than those comprising pure polymer. The temperature coefficients of viscosity of the first four oils in this table correspond to apparent activation energies of 16.5 to 11.5 kilocalories per mole; the other, more effective, diluents have activation energies in the range 11 to 3 kilocalories.

SUMMARY

A summary of the investigation with the three types of diluent can be made with reference to Table VI. Hydrocarbon oils are more effective low-temperature plasticizers the lower their temperature coefficient of viscosity. Dibutyl

Table VI

Viscosity and Compatibility Effect on ΔT_g of GR-S

Diluent	$\frac{\Delta(\log \text{ visc.})^a}{\Delta(1/T)}$	Vol. increase on swelling GR-S (%)	Max. ΔT_g[b] (° C)
Hydrocarbon	$2.5 \rightarrow 3.6 \times 10^3$	30 → 77	nil or small
Oils	1.6 → 2.4	59 → 82	6 → 9
Dibutyl sebacate	0.86	110	9
Tributoxylethyl phosphate	1.02	36	16
Dibutyl phthalate	1.02	66	24
Dioctyl adipate	1.00	100	37
Dioctyl sebacate	1.08	104	38
Hydrocarbon oils	0.69 → 0.85	215 → 265	> 25 → 30

[a] Kinematic viscosities at 100° and 210° F.
[b] Depression of glass transition temperature.

sebacate is representative of crystallizing diluents. Such compounds are ineffective low temperature plasticizers unless, (a) at equilibrium, favorable thermodynamic parameters permit their existence as liquids in the polymer, or (b) the plasticizers tend to exist as the nonequilibrium, supercooled, liquids in the transition temperature region of the polymer. Particularly desirable are liquids with low apparent activation energies of viscosity and high miscibility with polymer. The four ester plasticizers, tributoxyethyl phosphate, dibutyl phthalate, dioctyl adipate, and dioctyl sebacate, have temperature coefficients of viscosity corresponding to a virtually common activation energy of 4.5 kilocalories. Here, the magnitude of diluent-polymer interaction, as indicated by volume increase measurements, dictates the order of effectiveness of the ester.

SYNOPSIS

Glass temperatures (T_g) of pure and plasticized elastomers have been obtained from dilatometric measurements and from the temperature dependence of angular response to torsional stress. The depression of T_g by a diluent, determined by either method, is a convenient measure of its plasticizing ability. Some compounds which are normally crystalline above T_g of the pure polymer, but nevertheless are compatible with the polymer, depress the glass temperature. The polymer-diluent compatibility at low temperatures results either from supercooling, the depression of the melting point of diluent by polymer, or possibly a combination of both phenomena. T_g decreases as the diluent loading increases to a more or less well defined limit, beyond which further dilution has a negligible effect. For diester type plasticizers, both $\Delta T_{g\max}$ and the limiting diluent concentration are linear functions of compatibility, as defined by the extent to which standard polymer vulcanizates are swollen by plasticizer. The viscosities and apparent activation energies for flow (E_v) of hydrocarbon oils correlate with their low-temperature plasticizing efficiencies. Pour points and glass temperatures may also be significant properties of the diluents. It is concluded that low E_v and high solvency for polymer are desirable properties for low-temperature plasticizers.

ACKNOWLEDGMENTS

The author appreciates the permission extended by Polymer Corporation Limited to publish these data. The dilatometric measurements were made by R. L. Arblaster. Gehman measurements were made by J. E. Durley under the supervision of A. C. MacLeod. The author is indebted to L. A. McLeod and H. Leverne Williams for helpful discussions.

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[14] *Paraffinic, naphthenic,* and *aromatic* are relative terms, denoting the preponderance of straight-chain, naphthenic, or conjugated ring structures in the molecular mixture. The paraffin oil, for example, is dewaxed, but contains a large fraction of carbon atoms in straight chains attached to cyclic nuclei, conjugated or otherwise.

DYNAMIC FATIGUE OF RUBBER AND THE MECHANISM OF FAILURE BY REPEATED DEFORMATIONS *

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Dynamic fatigue is the reduction of the maximum tensile strength of a material by repeated periodic loads or deformations. The dynamic fatigue of vulcanized rubber[1] is basically the result of chemical oxidation processes, destruction during repeated deformations taking place by rupture of the chains throughout the rubber as a result of mechanically activated chemical processes. Physical factors also influence dynamic fatigue. However, the question of the nature and mechanism of dynamic fatigue of vulcanized rubber has not yet been explained; nor has the relation between fatigue and tensile strength of rubbers been clarified. The results of studies which make it possible to establish the fundamental laws of dynamic fatigue of rubbers and the destruction mechanism during repeated deformations are presented below.

Two widely used sinusoidal systems of repeated deformation were studied: (1) constant (maximum) elongations or deformations, ϵ = const.; (2) constant (maximum) loads or conventional stress, f = const. The number N of cycles before failure and the time before breaking, or the life of a specimen, were determined in these tests. In the first system, the breaking load, fixed by the apparatus, was less than the initial maximum load, owing to the process of "dynamic relaxation", and in the second system they were equal. The breaking load divided by the initial cross-section and the cross-section at break gives, respectively, the conventional f and the true dynamic tensile strength σ of the specimen.

Considerable variation in the measured values was observed from specimen to specimen. For this reason the dynamic tensile strength, the number of cycles, and the time before failure were determined from the average of 15–20 experiments. The data in Figures 1–4 refer to an unloaded butadiene-styrene copolymer vulcanizate of SKS-30A (temperature[2] of the specimens 30° C).

For both systems, the nature of the relation between the number of cycles and the maximum deformation, frequency, and temperature is the same. The relation of the number of cycles to the deformation is shown in Figure 1. For the first system, the initial maximum deformation is at the same time the deformation at rupture; for the second, the initial and rupture deformations differ, as a result of extension of the specimen under the influence of the load. Accordingly, on the graph for the system, f = const., two characteristics are drawn.

It is seen from Figure 1 that the severity of a testing system depends on the method of comparison. Comparing the systems at equal initial maximum deformations, we see that the second system is more severe, whereas at equal rupture deformations, on the other hand, the first system is more severe.

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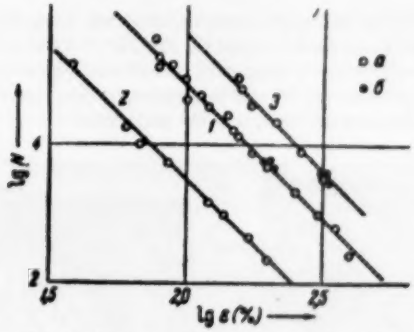

FIG. 1.—Number of cycles before failure as a function of the maximum deformation. Curve 1—When ϵ is constant, Curves 2 and 3—When f is constant. Curve 2—For initial maximum deformation. Curve 3, —For rupture deformation a at frequency 256 min.$^{-1}$, b at frequencies 88, 200, and 560 min.$^{-1}$. Specimens were 1 mm. thick.

The following relation holds between the number N of cycles before failure and the deformation ϵ for both systems:

$$N \cdot \epsilon^{\gamma} = B \tag{1}$$

where ϵ is the given (maximum) deformation for the first system[3], and the initial (maximum) or rupture deformation for the second system[3]. In the interval studied, both constants γ and B, are independent of the frequency; and γ is also independent of the temperature and testing system.

For the second system, using the formula: $\sigma = E \cdot \epsilon$, which is accurate in the entire range of applied maximum deformations and stresses, instead of Equation (1) we obtain:

$$N \cdot \sigma^{\gamma} = C \tag{2}$$

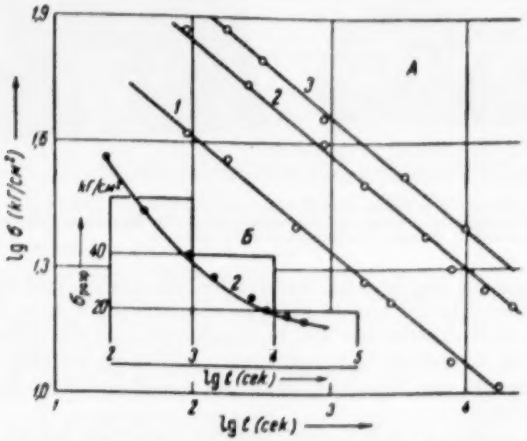

FIG. 2.—Characteristics of fatigue in rubber (true tensile strength—life) in various systems. Line 1—Dynamic, with ϵ constant, Line 2—Dynamic with f constant (A and B), Line 3—Static, with f constant. The abscissa indicates log t in seconds; the ordinate log σ in kg. per sq. cm. The symbols within the diagram represent $\sigma_{rupture}$ in kg. per sq. cm. The symbols within the diagram represent $\sigma_{rupture}$ in kg. per sq. cm, and log t in seconds.

where σ is either the initial maximum or the true dynamic tensile strength. Equation (2) has the same form as that for metals[4]. This reflects the similarity in the general characteristics of fatigue in metals and vulcanized rubber, despite the difference and peculiarity of the relaxation properties and rupture mechanisms of high-elastic and ordinary elastic materials.

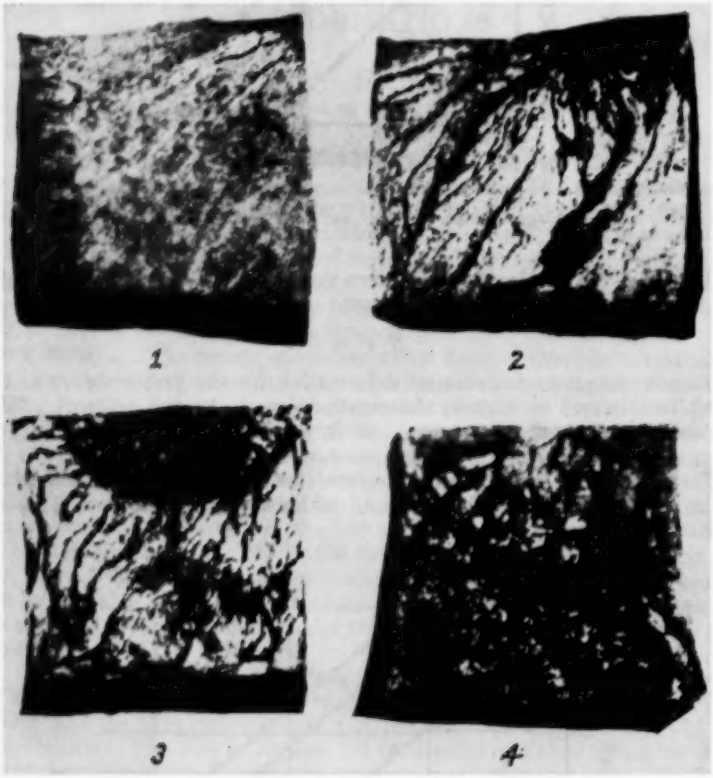

FIG. 3.—Rupture surfaces of specimens with cross-section 6 × 6 mm., tested with repeated stretching (ϵ = constant). Photograph 1—Maximum deformation 200%, life 3 minutes; Photograph 2—150%, 1 hour; Photograph 3—100%, 2 hours; Photograph 4—50%, 40 hours.

The dynamic life and dynamic tensile strength of vulcanized rubber are of a statistical nature, like the tensile strength of brittle substances; this is due to deviations in such experiments and the dependence of the dynamic life and strength on the conditions of measurement. With an increase of thickness, the tensile strength and life of rubber which is well protected from oxidation processes decrease.

The static fatigue of rubber, glass, and other materials follows the relation:

$$\log \sigma = a - b \cdot \log t \qquad (3)$$

where σ is the true rupture stress and t the life.

The relation is analogous for the dynamic fatigue of rubber (see Figure 2. A—in logarithmic coordinates; B—in semilogarithmic). The characteristics of static and dynamic fatigue of rubber (Figure 2A) have the same value for b and different values for a. The constant b does not depend on the experimental temperature and deformation system, but on the frequency of deformation ν (static regime $\nu = 0$).

Equation (2) and (3) are equivalent and coincide if, considering that $N = \nu t$, we assume that $a = \frac{1}{\lambda} \log \frac{C}{\nu}$ and $b = \frac{1}{\lambda}$. Since $b \ll 1$, a small change of tensile strength σ is accompanied by greater changes in the life t. Consequently, the life is a more sensitive characteristic of fatigue in vulcanized rubber than is the tensile strength. For this reason technologists use the "durability" of rubber, and not the tensile strength, as a characteristic of dynamic fatigue.

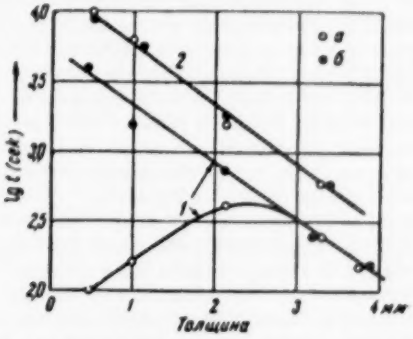

FIG. 4.—Influence of thickness of specimen on life during (1) dynamic and (2) static tests of rubber (a) poorly and (b) well protected from oxidation.

The mechanism of rupture of vulcanized rubber is different from that of ordinary solids. Failure of rubber during dynamic, as well as static[5], tests takes place through the formation of surface cracks (cuts), and is characterized by two stages (slow and rapid).

It is seen from Figure 3 that rapid rupture gives a smooth glossy surface, while slow rupture gives two zones of ruptured surface area. In this type of failure (elastic) in the slow stage, a rough zone is formed, and in the rapid stage, a smooth glossy one, while, in the rupture of ordinary solid materials, the order of these zones is reversed. The mechanism of destruction in the slow stage[5] is characteristic of polymers.

The formation of surface cracks in rubber as well as cracks in brittle materials takes place through the chemical bonds. In brittle substances, rupture of the chemical bonds is usually purely mechanical. Rupture of the chains of a polymer can be both physical and chemical.

It follows from this that (1) the laws of dynamic and static fatigue of vulcanized rubber are the same; (2) there is no basic difference in the failure mechanism of rubber in dynamic and static tests; (3) fatigue in rubber is a physical process of destruction of the material under the influence of static or alternating loads.

A static system is less severe then a dynamic one for testing both rubber and metals. Despite the fact that, in a static system, the rubber is under constant

stress, its failure takes place much later than in dynamic tests, where the rubber is under stress only part of the time. This is explained, first, by the fact that, with periodic loads, the excess strains at the micro-flaws cannot entirely relax during each loading cycle, while with a static load they are equalized and approach a uniform value; second, because the failure of polymers during repeated deformations is accelerated by mechanically activated chemical processes[6]. The latter distinguish fatigue in rubber from fatigue in metal.

Rubber poorly protected from oxidation processes gives an anomalous relation between the life and the thickness of the specimen. Figure 4 shows that the life of well-protected rubber increases with decrease of thickness, whereas poorly protected rubber gives an analogous relation only at great thicknesses, while at small thicknesses its life falls sharply. (With a decrease in the maximum deformation the position of the Y (Figure 4) is displaced toward the greater thickness.) In static tests, both types of rubber give the same results.

It follows that: (1) in static systems, rupture of the chains is basically a physical process and in dynamic systems a combined (physico-chemical) process; (2) in the presence of chemical processes, failure of a rubber is characterized by the same changes as in their absence, only the changes are more rapid.

The better a rubber is protected, the more constant is a and the closer are the characteristics of dynamic fatigue to those of static fatigue. The constant b does not depend on the type of protective agent, the density of the spatial network, or the type of accelerator, but on the nature of the rubber and the filler. This result, however, requires further confirmation. The independence of the constant b from chemical processes, the identity of the mechanisms of failure, and the laws of fatigue in rubber during static and dynamic tests indicate that the elementary formation of rupture centers has a common mechanism in both cases. Chemical processes have an essential role in the acceleration of the formation of failure nuclei or flaws. In dynamic tests, the role of the chemical processes is so much greater that in many cases they determine the life of rubber products.

The results of the study show that the physical-chemical processes of failure of ordinary materials are similar to the dynamic fatigue of rubber.

ACKNOWLEDGMENT

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APPLICATION OF RADIOACTIVE SULFUR TO THE STUDY AND CONTROL OF THE VULCANIZATION PROCESS *

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Ordinarily the kinetics of the vulcanization process is controlled by the proportion of combined sulfur, which is determined by the method of oxidation with nitric acid and bromine, the method of fusion with metallic potassium and magnesium, and other methods.

A considerable increase of the rapidity and accuracy of the determinations may be achieved if labeled sulfur, containing the isotope S^{35}, is used as the vulcanizing agent. The half-life of this isotope is 87.5 days, and the energy of the β-particles amounts to 0.17 Mev. The combined sulfur content is determined from the intensity of the β-radiation.

The method which we developed can be described as follows. A rubber stock, containing labeled sulfur of known radioactivity, is mixed on a laboratory mill. A sheet of this rubber stock, wrapped in cellophane, is vulcanized in a press at a given temperature and pressure. The thickness of the sheets should not be less than the maximum length of the path of β-particles in the rubber. For a soft rubber, this thickness amounts to 0.3 mm.

Circular pieces are cut out of this vulcanized sheet with a skiving knife; these are 20 mm. in diameter, which is close to the size of the window of the Geiger-Müller end-window counter. The samples are treated with hot acetone for a period of 50 hours in order to remove the free sulfur, and then are dried. For the radioactivity measurement, a plexiglass disk, with a depression in the center the same size as the sample, is used. The sample is covered by a round aluminum shield, with a hole in it about 0.15 mm. in diameter. The radioactivity is measured on the surface of both sides of the vulcanizate, and an average of four samples is taken (from eight determinations).

In order to obtain a calibration curve, a set of samples of rubber stocks containing from 0.5 to 3.0 per cent of radioactive sulfur by weight were prepared. The radioactivity of the samples obtained was measured with a strict adherence to the conditions described above. The radioactivity of the elemental sulfur used for vulcanization was determined after its oxidation by the Carius method, in the form of benzidine sulfate.

In constructing the calibration curve (Figure 1), the ordinate axis is made to represent the relative radioactivity at the surface of the vulcanizate (or raw rubber) in relation to the relative radioactivity of the sulfur preparation, both being measured under the same geometric conditions. The abscissa represents the sulfur content of the samples.

We determined the combined sulfur content on vulcanizates of butadiene-styrene rubber (SKS-30) with three types of accelerators: diphenylguanidine,

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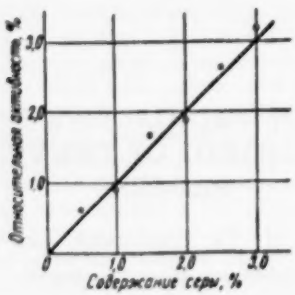

FIG. 1.—Calibration curve. The abscissa represents the percentage by weight of combined sulfur; the ordinate the relative radioactivity in percent.

mercaptobenzothiazole, and sulfenamide-BT at various stages of vulcanization. Parallel determinations of the combined sulfur by the method of oxidation with nitric acid and bromine were carried out. Data from both methods agree well (Figure 2).

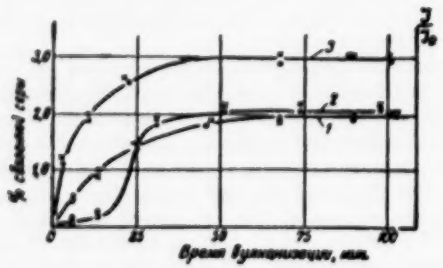

FIG. 2.—Curves of vulcanization kinetics. 1—With the accelerator diphenylguanidine; 2—With the accelerator sulfenamide-BT; 3—With the accelerator mercaptobenzothiazole (×-×—analytical data; ○-○—data from radioactivity measurement). The abscissa represents time of vulcanization in minutes; the ordinate the percentage of combined sulfur.

The time necessary for a determination of combined sulfur on each sample of radioactive vulcanizate amounts to 8–10 minutes (not counting the time involved in extracting the free sulfur). The average error in the determinations was less than 1 per cent.

Application of this method is possible, not only in research, but also in industrial control work.

SULFUR EXCHANGE REACTIONS IN VULCANIZED RUBBER *

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In one of our previous works[1] we have shown that vulcanization structures contain mono-, di- and polysulfide bonds between the molecular chains of the rubber. The concentration, proportion, and distribution of these various bonds depend on the type of rubber and the conditions of vulcanization, but mainly on the nature of the curatives. Inasmuch as the vulcanization structures determine in large degree the physical, chemical, and mechanical properties of the vulcanizate, the different methods which enable us to determine the types of sulfide bonds in the vulcanizate are very important. Among the chemical methods applied for this purpose are the reactions of sodium sulfite[1] and of methyl iodide[2] with the vulcanizate.

Of great interest in research on the nature of sulfur bonds in vulcanizates is the method of exchange reactions with radioactive sulfur; since sulfur, as numerous experiments have shown, diffuses easily in rubber, thus insuring the possibility of carrying out exchange reactions without having to get the vulcanizate into solution.

The work of Guryanova and coworkers[3] has shown that sulfur which is located in the central position in polysulfide compounds (R—C—S—S*—S—C—R) goes readily into an isotope exchange with the labeled sulfur, at 100°–120° C. On the other hand, sulfur atoms bonded directly to the carbon atoms do not take part in an exchange reaction under these conditions. The mobility of sulfur atoms depends on the type of groups adjacent to them.

Analogously with the above-mentioned phenomenon, one might expect that the sulfur in polysulfide bonds of vulcanized rubbers would enter more or less readily into an isotope exchange with the radioactive sulfur, while at the same time the sulfur situated in mono- and disulfide bonds would not exchange. Hence from the intensity of the exchange of combined sulfur in a vulcanizate, information may be obtained about the relative sulfur content of the polysulfide bonds.

The method which we used in carrying out exchange experiments was as follows. Into an ampoule was placed 0.35 gram of the ground-up vulcanizate and radioactive sulfur in such amounts that the ratio of inactive sulfur in the vulcanizate to the radioactive sulfur added amounted to 1:1.62, 1:3.1 and 1:1.25, respectively, in parallel series of experiments. The vulcanizate had previously been extracted with cold acetone for a period of 100 hours in order to remove the free sulfur. The ampoule was evacuated to a residual pressure of 10^{-5} to 10^{-6} mm. of mercury. Then 15 ml. of toluene, which had been deaerated and saturated with nitrogen, was drawn into the ampoule, after which it was sealed up and heated in a constant-temperature oil bath at $130 \pm 1°$ C for various lengths of time.

* Translated for Rubber Chemistry and Technology by Malcolm Anderson from *Doklady Akademii Nauk SSSR*, Vol. 99, No. 5, pages 819–822 (1954).

Under the above conditions, with heating for 10 hours at 130°, no more than 2.7 per cent of the vulcanizate went into solution. The combined sulfur content of the samples was then determined by the Carius method, and the radioactivity of the sulfur was determined in the form of benzidine sulfate.

The experimentation was carried out on two butadiene-styrene vulcanizates, one of which had, as its curatives, sulfur (4 parts by weight per 100 parts of rubber), diphenylguanidine (1 part), and zinc oxide (5 parts); while the other had tetramethylthiuram disulfide (3 parts) and zinc oxide (5 parts). Such a

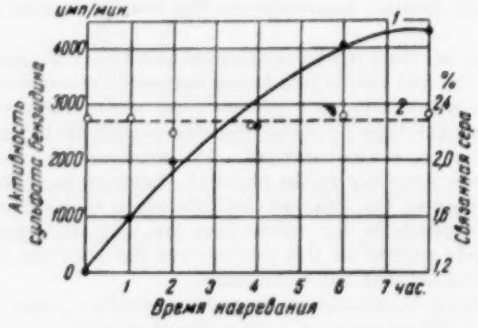

FIG. 1.—Kinetics of exchange (*1*) and of sulfur combination (*2*) in a vulcanizate with diphenylguanidine. The abscissa represents the period of heating in hours; the ordinate at left represents the radioactivity of the benzidine sulfate in impulses (counts) per minute, while that at right represents the percentage of combined sulfur.

difference in the composition of the curatives insures, as we showed earlier[1], a marked difference in the nature of the vulcanization bonds: the vulcanizate with diphenylguanidine contains mainly polysulfide bonds, while the one with tetramethylthiuram disulfide has mono- and disulfide bonds.

Figure 1 presents the kinetics of the exchange reaction in a vulcanizate with diphenylguanidine, where the ratio between inactive (combined) and radioactive (free) sulfur is 1:6.2. The parallel analysis of the combined sulfur which was carried out showed that no combination of sulfur with the vulcanizate had

TABLE 1

Ratio of combined to radioactive sulfur	Kinetic constant at 130° C ($K \times 10^3$ per min.$^{-1}$)	Exchange (%)
1:6.2	1.58	32.4
1:3.1	1.12	37.2
1:1.25	0.537	32.2
		Average 33.9

taken place under the conditions of the test. Thus the increasing radioactivity of the sulfur in the vulcanizate is explained entirely by an exchange reaction between the vulcanization sulfur structures and the labeled sulfur. The kinetics of the exchange conforms to an equation of the first order[4]; but the dependence which the kinetic constant was found to have on the concentration of radioactive sulfur (see Table 1) indicates a more complex reaction mechanism. The amount of combined sulfur entering into the isotope exchange does not depend on the ratio between radioactive and inactive sulfur, and amounts to

33.9 per cent on an average. This amount agrees with the quantity of sulfur extracted from the vulcanizates under investigation by boiling with a 10 per cent aqueous solution of sodium sulfite[1]. Such an agreement gives a good indication that in an exchange reaction, as in the reaction with sodium sulfite, it is the central atoms of polysulfide bonds of the type R—C—S—S*—S—C—R that take part.

A different situation is found in the reaction between labeled sulfur and a vulcanizate obtained with tetramethylthiuram disulfide as the vulcanizing agent. In this case, the increase of radioactivity as the vulcanizate is heated parallels the combination of the labeled sulfur with the vulcanizate. A linear relation was found between the amount of sulfur combined and the radioactivity of the vulcanizate sulfur (see Figures 2 and 3). Therefore the thiuram vulcanizate does not contain sulfur in such a form as would enter into an isotope exchange at 130° C with elemental sulfur. This also agrees fully with research carried out earlier[1], according to which thiuram vulcanizates contain no poly-

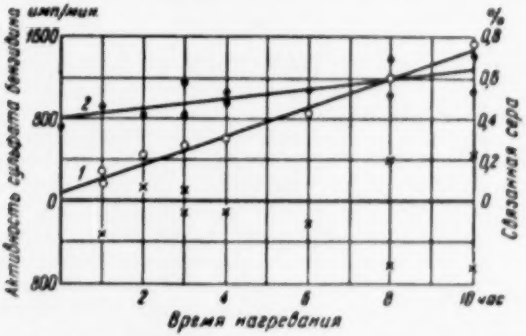

FIG. 2.—The kinetics of the increase of radioactivity (*1*) and of sulfur combination (*2*) in a vulcanizate with thiuram. The point ● indicates the radioactivity of the combined sulfur, corrected for the radioactivity of the sulfur added. The abscissa represents the period of heating in hours. The ordinate at left represents the radioactivity of the benzidine sulfate, in impulses per minute; that at right represents the percentage of combined sulfur.

sulfide sulfur, but instead contain monosulfide bonds (R—C—S—C—R) and possibly disulfide bonds, R—C—S—S—C—R. The absence of any exchange of labeled sulfur with thiuram vulcanizates likewise allows us to draw the preliminary inference that when the thiuram decomposes under vulcanization conditions, then, despite the contrary findings of Craig[5], radicals of the type CH_3

$\diagdown$
N—C* either are not formed at all or else the combination of these with the
$\diagup$ ‖
CH_3 S

rubber molecules at the double bonds causes the sulfur atom to be stabilized. It is known, for example, that nickel diethyldithiocarbamate is not able to exchange with elemental sulfur at 140° C.[3]

The exchange of sulfur atoms takes place, not only between elemental free sulfur and the vulcanization structures, but also within the vulcanization structures themselves. The following experiments demonstrate this phenomenon. Vulcanizates were prepared containing diphenylguanidine as the accelerator, with labeled sulfur in one case, and regular sulfur in the other. The vulcanizates

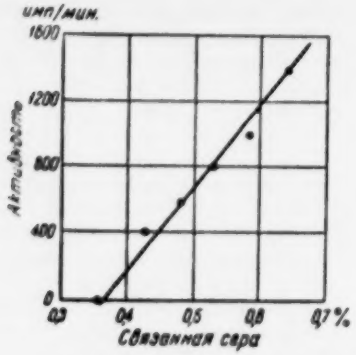

FIG. 3.—The dependence of the increase of radioactivity on the amount of combined sulfur, in a vulcanizate with thiuram. The abscissa represents the percentage of combined sulfur; the ordinate the radioactivity in impulses per minute.

were extracted with acetone to remove the free sulfur completely. After this, sheets of vulcanizates containing labeled sulfur were laid together with sheets of vulcanizates containing regular sulfur, and were pressed together with a clamp in such a way that air was excluded as completely as possible from the contact surfaces of both sheets. The assembled sheets were heated in a reactor at a temperature of 130° C. After the heating, the sheets were separated, and their radioactivity was determined both on the side of the contact surface and on the opposite side (in the non-radioactive vulcanizate)[6]. As we can see from the data presented in Figure 4, the vulcanizate with regular sulfur becomes radioactive, and, at the same time, the increase of this radioactivity on the side in contact with the radioactive vulcanizate (curve *3*) corresponds to the decrease of the radioactivity of the latter on that side (curve *1*). Such an exchange of sulfur atoms between the two vulcanizates could have resulted either from the intermolecular reaction of two colliding polysulfide groups of different

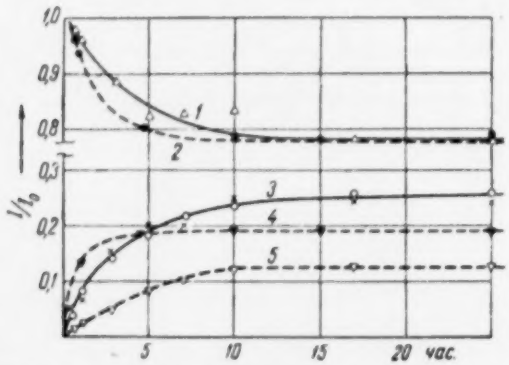

FIG. 4.—The change of the radioactivity of a vulcanizate with diphenylguanidine: *1*—radioactive vulcanizate; *3*—original vulcanizate on the contact side; *5*—original vulcanizate on the other side. The change of radioactivity of a vulcanizate which was swelled in a solution of diphenylguanidine: *2*—radioactive vulcanizate; *4*—original vulcanizate on the contact side. The abscissa represents time in hours; the ordinate the intensity of radioactivity, relative to the original intensity.

vulcanizates[3] or else from the cleavage of sulfur radicals and their change of positions and subsequent attachment onto the vulcanization structure.

In order to ascertain the possibility of the latter mechanism, the following experiment was carried out. Between sheets of the radioactive and of the regular vulcanizate was inserted a layer of polyisobutylene varying from 0.2 to 0.9 mm. thick. The presence of such an intermediate layer of polyisobutylene with a thickness up to 0.9 mm. did not prevent entirely the occurrence of exchange under the conditions given above, although the degree of exchange was sharply reduced; and the thicker the intermediate layer, the greater the reduction. Thus, with an immediate contact between vulcanizates, the exchange caused a loss of up to 25 per cent of the radioactivity of the labeled sulfur vulcanizate at the equilibrium point (16 hours); while with an intermediate layer of polyisobutylene 0.34 mm. thick in place, the loss of radioactivity after 25 hours amounted to 2.3 per cent. The degree of exchange is lowered likewise if, after the free sulfur is removed, a vulcanization accelerator is introduced anew into the radioactive vulcanizate, this being diffused by means of swelling the vulcanizate in a solution of the accelerator (Figure 4, curves *2* and *4*).

The facts noted above bear witness that the exchange takes place basically through a direct reaction between polysulfide groups. The diffusion of sulfur groups was exhibited only in a negligible degree.

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[1] Dogadkin and Tarasova, *Doklady Akad. Nauk SSSR* **85**, 1069 (1952); *Kolloid. Zhur.* **15**, 347 (1953).
[2] Selker and Kemp, *Ind. Eng. Chem.* **36**, 16 (1944); Dogadkin, Karmin, and Stukolova, "Investigations in the Physics and Chemistry of Rubbers", M., **1950**, p. 59.
[3] Guryanova, *Zhur. Fiz. Khim.* **28**, 67 (1954).
[4] Craig, Rubber Chem. & Technol. **24**, 262 (1951).
[5] Brodskil, "The Chemistry of Isotopes", **1952**, p. 240.
[6] The procedure mentioned is described in a previous paper (cf. Bresler, *Zhur. Tekh. Fiz.* **24**, 4 (1954)).

MOBILITY OF SULFUR IN SULFUR-CARBON BONDS, AND THE MECHANISM OF THE ACTION OF RUBBER-VULCANIZATION ACCELERATORS *

G. P. Miklukhin, A. F. Rekasheva, I. I. Kukhtenko, L. V. Sulima, I. P. Gragerov, and G. A. Blokh

The mechanism of the action of rubber-vulcanization accelerators is unknown, and yet they are used so extremely widely in practice that commercial production of rubber would now be unthinkable without the use of accelerators.

Most accelerators are sulfur-containing compounds. As our ultimate aim was the elucidation of the mechanism of the action of accelerators, we decided that we should first of all establish whether or not the accelerating action is associated with the mobility of the sulfur contained in the accelerator.

In themselves, many accelerators are unable to effect the vulcanization of rubber in absence of elementary sulfur. On the other hand, elementary sulfur vulcanizes rubber slowly, even in absence of accelerators. It follows that accelerators activate sulfur in some way. It is natural to suppose that accelerators form intermediate compounds or complexes with sulfur, the decomposition of which results in the elimination of sulfur in an active condition. This idea is far from new, but no direct data on the interaction of accelerators with sulfur have been reported.

It might be expected that the study of exchange reactions of sulfur isotopes between free sulfur or the sulfur of hydrogen sulfide, on the one hand, and sulfur-containing compounds, on the other, would permit an approach to be made to the solution of this problem. If, indeed, such reactions occur, so that exchange occurs between the sulfur of organic compounds and free sulfur, then this must provide evidence of chemical interaction between components of the mixture. A study of the kinetics of isotopic exchange in such systems may help to establish the ways in which the intermediate compounds are formed, and the structures and other characteristics of these compounds.

The investigation of isotopic-exchange reactions of sulfur is of interest for its own sake, since it provides new information about the mobility of sulfur in organic compounds, the chemistry of which has received very little study. As subjects for investigation we selected organic compounds containing sulfur in various forms of combination with carbon and other elements. The results of investigations on the exchange reactions of sulfur—carried out both in our own laboratory and in others—are given in Table 1.

The results given in Table 1 indicate that sulfur present in organic compounds in the groupings, C—S—H, C—S—C, and C—S—S—C, is unable to undergo exchange with free sulfur or the sulfur of hydrogen sulfide, even under very severe conditions. On the other hand, according to Syrkin and coworkers[1], the central sulfur atom (which is not linked to carbon) of trisulfides is extremely

* From the *Proceedings of the Conference of the Academy of Sciences of the USSR on Peaceful uses of Atomic Energy*, July 1–5, 1955, Session of the Division of Chemical Science, pages 153–162. Except for the Summary, which is transcribed from the Russian publication, this translation was made by the Consultants' Bureau of New York.

TABLE 1

SULFUR EXCHANGE IN VARIOUS BONDS

Reacting compounds	Reaction conditions	Results of reaction	Authors of work
1	2	3	4
The bond C—SH			
S^{*} + $N{\equiv}C{-}S{-}NH_4$	115°, solution in mixture of isopentyl alcohol and xylene	No exchange in 5 hours	Kukhtenko and Miklukhin[4]
S^{*--} + NCS^-	0°, aqueous solution	No exchange in 47 hours	Adamson and Magee[5]
H_2S^{*} + $HSCH_2COOH$	100°, aqueous solution	No exchange in 6 hours	Tuck[6]
$HSCH_2{-}CH(NH_2){-}COOH$ + H_2S^{*}	100°, aqueous, acid, or alkaline solution	No exchange in 6 hours	Tuck[6]
H_2S^{*} + C_6H_5SH	175°, without solvent, and also in aqueous acid and alkaline solutions	No exchange in 14 hours	I. P. Gragerov, present investigation
H_2S^{*} + p-HOC_6H_4SH	175°, without solvent	No exchange in 14 hrs., nor in 3 hrs. at 130° in aq. alkaline soln. At 165° in *N* aq. NaOH or *N* aq. HCl: partial decomposition	I. P. Gragerov, present investigation
H_2S^{*} + m-HOC_6H_4SH	175°, without solvent	No exchange; also at 129° for 3 hrs. in *M* aq. HCl. Under more severe conditions: partial decompn.	I. P. Gragerov, present investigation
H_2S^{*} + o-$HOOC{-}C_6H_4{-}SH$	175°, without solvent or in aqueous acid or alkaline solution	No exchange in 14 hours	I. P. Gragerov, present investigation
The bond C=S			
S^{*} + $(NH_2)_2C{=}S$	118°, solution in a mixture of isopentyl alcohol and xylene	Complete exchange in 2.5 hours. 80% exchange in 9 hours at 135° in isopentyl alcohol.	Kukhtenko and Miklukhin[4]; Blokh, Golubkova, and Miklukhin[7]; Guryanova[8]

TABLE I (continued)

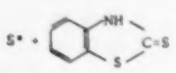
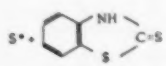
Reacting compounds	Reaction conditions	Results of reaction	Authors of work
1	2	3	4
$H_2S^* + (NH_2)_2C{=}S$	100°, aqueous acid or alkaline solution	No exchange in 6 hours	Guryanova[8]
$S^* + CS_2$	100°, without solvent	No exchange in 68 hours	Cooley et al.[9]
$H_2S^* + CS_2$	120°, benzene solution	No exchange in 95 hours	Douglas et al.[10]
$S^* + C_6H_5NHC(=S)NH_2$	137°, solution in xylene	30% exchange in 7.5 hours. Complete exchange in 18 hours	Guryanova[8]
$S^* + (C_6H_5NH_2)C{=}S$	137°, solution in xylene	80% exchange in 22 hours	Guryanova[8]
$H_2S^* + H_2N{-}C(=S){-}NH{-}CH_2{=}CH{-}CH_2$	100°, aqueous solution	No exchange in 6 hours	Tuck[6]
$Na_2S^* + CH_4C(=S)NH_2$	100°, aqueous solution	No exchange in 4 hours	Guryanova[8]
	154°, melt	Almost complete exchange of peripheral sulfur in 3 hours. No exchange of sulfur in the ring. Intensive exchange of sulfur in the presence of rubber during the vulcanization process.	Blokh, Gloubkova, and Miklukhin[11]
	131–181°, in naphthalene	The kinetics of the exchange of peripheral sulfur were studied, also the dependence of k' on the concentrations of reactants and the effect of the solvent. E = 24 kcal/mole. In toluene solution $k'_{155°} = 365.10^{-3}$ hour^{-1}; $\tau_{\frac{1}{2}} = 2$ hours.	E. N. Guryanova[12]; L. V. Sulima, A. F. Rekasheva, G. P. Miklukhin, present investigation.

TABLE 1 (continued)

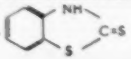
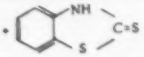
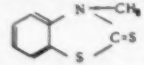
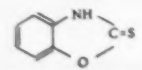
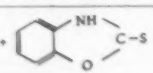
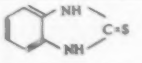
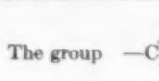
Reacting compounds	Reaction conditions	Results of reaction	Authors of work
1	2	3	4
H_2S^* + 	135° and 150°, in toluene	$k'_{135}° = 39 \cdot 10^{-3}$ hour^{-1} $k'_{150}° = 117 \cdot 10^{-3}$ hour^{-1} E = 25 kcal/mole	A. F. Rekasheva, G. A. Blokh, G. P. Miklukhin, present work
Na_2S^* + 	100°, aqueous solution	No exchange	Guryanova[8]
S^* + 	150°, solution in a mixture of toluene and alcohol	$\tau_{\frac{1}{2}}$ = 6 hours	I. L. Gankina, G. P. Miklukhin, present work
S^* + 	135°, solution in a mixture of toluene and alcohol	$k'_{135}° = 9 \cdot 10^{-3}$ hour^{-1} $k'_{150}° = 47 \cdot 10^{-3}$ hour^{-1} E = 27 kcal/mole	L. V. Sulima, A. F. Rekasheva, G. P. Miklukhin, present investigation
H_2S^* + 	150°, solution in toluene	$k'_{150}° = 48 \cdot 10^{-3}$ hour^{-1}	A. P. Rekasheva, G. A. Blokh, G. P. Miklukhin, present work
S^* + 	150°, solution in a mixture of toluene and alcohol	$k'_{135}° = 2 \cdot 10^{-3}$ hour^{-1} $k'_{150}° = 18 \cdot 10^{-3}$ hour^{-1} E = 34 kcal./mole	A. P. Rekasheva, G. A. Blokh, G. P. Miklukhin, present work
The group 			
$S^{*--} + CS_3^{--}$	30°, aqueous solution, pH 9	$\tau_{\frac{1}{2}}$ = 40 minutes	Edwards[12]
$S^{*--} + CS_2$	30°, aqueous solution of sulfide: two-phase system	Exchange occurs	Edwards[12]

TABLE 1 (continued)

Reacting compounds	Reaction conditions	Results of reaction	Authors of work
1	2	3	4
$S^{*--} + CH_3CSOH$	125°, without solvent	Complete exchange in 1.5–2 hours	Foka and Burkser[14]
$S^* + C_2H_5OCSSK$	0°, solution in mixture of alcohol and toluene	Both sulfur atoms undergo exchange; $k'_0° = 0.024$ min^{-1}; $k'_{16}° = 0.108$ min^{-1}; In a solution of $CS_2 + C_2H_5OH$ $k'_{20}° = 0.132$ min^{-1} The rate constant does not change when the concentration of reactants is reduced to one-third	Foka and Burkser[14]
S^* + nickel xanthate	139°, solution in benzene	$k'_{139}° = 0.071$ hour^{-1}; $k'_{150}° = 0.35$ hour^{-1}; exchange of 4 sulfur atoms	I. I. Kukhtenko, L. E. Burkser, G. P. Miklukhin, present investigation
$S^* + C_2H_5OCSSK + CS_2$	100°, solution in ethanol	Complete exchange of sulfur in all three components	Foka and Burkser[14]
$S^* + (C_2H_5)_2NCSSNa$	50°, solution in mixture of alcohol and toluene	$k'_{50}° = 0.032$ hour^{-1}; $k'_{60}° = 0.084$ hour^{-1}; $k'_{70}° = 0.24$ hour^{-1} E = 22 kcal/mole	Kukhtenko and Miklukhin[4]
$S^* + (C_2H_5)_2NCSSNa$	60°, solution in isopentyl alcohol	Complete exchange in 1.5 hours. Complete exchange in xylene in 5 hours at 100°	Guryanova[8]
S^* + nickel diethyldithiocarbamate	140°, solution in xylene	No exchange in 7 hours	Guryanova[8]

TABLE 1 (continued)

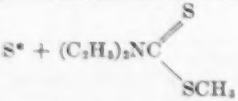
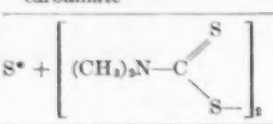
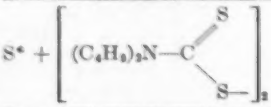
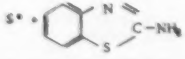
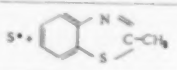
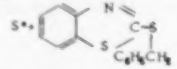
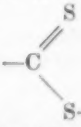
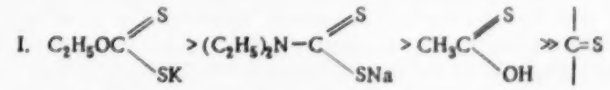
Reacting compounds	Reaction conditions	Results of reaction	Authors of work
1	2	3	4
S* + 	156°, solution in toluene	$k'_{144}° = 0.156$ hour^{-1}; $k'_{170}° = 0.915$ hour^{-1}; One sulfur atom undergoes exchange	I. I. Kukhtenko, L. E. Burkser, G. P. Miklukhin, present investigation
S* + zinc diethyldithiocarbamate	130°, in xylene	Slow exchange	Guryanova and Kuzina[15]
S* + 	126°, in naphthalene	Four sulfur atoms undergo exchange. The kinetics were studied. At 100° exchange proceeds in presence of rubber.	Blokh, Golubkova, and Miklukhin[16] Guryanova and Kuzina[15]
S* + 	130°, in naphthalene	Rate of exchange is close to that in the thiuram-sulfur system	Guryanova and Kuzina[15]
The group C—S—C			
S* • 	150°, melt	No exchange in 45 minutes	Blokh, Miklukhin, and Golubkova[17]

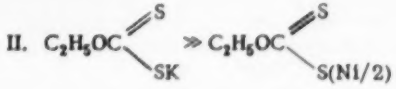
TABLE 1 (continued)

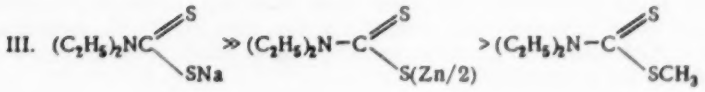
Reacting compounds	Reaction conditions	Results of reaction	Authors of work
1	2	3	4
	137°, melt	No exchange in 15 minutes	Blokh, Miklukhin, and Golubkova[17]
	150°, melt	No exchange in 3 hours	Blokh, Miklukhin, and Golubkova[17]
	The group C—S—S—C		
$S^* + (C_2H_5)_2S_2$	—	No exchange with sulfur bound to carbon in formation and breakdown of trisulfide	Guryanova, Syrkin, and Kuzina[1]
S^* + bis(2-benzothiazolyl) disulfide	138°, solution in xylene	Complete exchange of two sulfur atoms in 22 hours	Guryanova[3]
$[HOOC—C(NH_2)CH_2—S—]_2 + H_2S^*$	100°, aqueous acid or alkaline solution	No exchange in 6 hours	Tuck[4]
	The group C—S—S—S—C		
$S^* + (C_2H_5S)_2S$	100°, without solvent	Complete exchange of the central sulfur atom in 10 hours. The same at 200°. No exchange of sulfur in the C—S bonds	Guryanova[6]
$S^* + (p\text{-}CH_3C_6H_4S)_2S$	100°, solution in benzene	Exchange of the central sulfur atom	Guryanova[5]

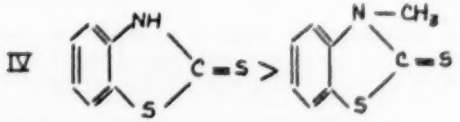
mobile. Sulfur of the thione group (C=S) of carbon disulfide is not labile, but in thiourea and its derivatives and in 2-mercaptobenzothiazole[2] it undergoes rapid exchange at 120–150°. Finally, sulfur in the group  undergoes extremely rapid exchange in potassium xanthate, but not so rapid in sodium diethyldithiocarbamate. Heavy-metal salts, and particularly the esters, of dithio acids contain sulfur of much lower mobility; it is similar in this respect to thione sulfur. Similar behavior was observed by Brodsky and coworkers in an investigation of oxygen-exchange reactions between water and organic compounds[3].

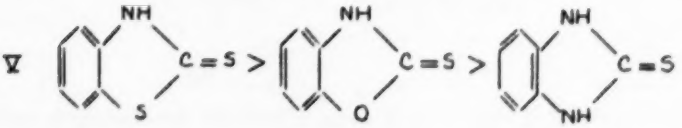
The compounds studied may be divided into several series according to the rate at which they undergo exchange with free sulfur:









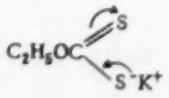


The results of these comparisons are in accord with the hypothesis that the mobility of sulfur depends on polarity, i.e., on the distribution of charge in the molecules, the mobility being the greater, the higher the polarity of the relevant sulfur-carbon link. This hypothesis is not a trivial one, for in some investigations exchange reactions of sulfur have been ascribed to radical mechanisms in which the homolytic rupture of carbon-sulfur bonds occurs.

The radical mechanism cannot be reconciled with the above-cited experimental data.

The truth of this inference is demonstrated by the variation in exchange

rate in series II and III. Owing to σ–π-conjugation, in potassium ethylxanthate:



the negative charge on the sulfur atom of the C=S group is great. If complete ionization occurred under the conditions of our experiments, then both sulfur atoms were equally negative. On the other hand, in nickel ethylxanthate—irrespective of its structure, which is probably that of a complex salt—the sulfur-nickel linkage is considerably more covalent, and the corresponding σ–π-coordination creates a considerably lower negative charge on the sulfur of the C=S group.

The change of the mobility of sulfur in salts and esters of diethyldithiocarbamic acid has the same origin. The conjugation of the bonds in the methyl ester is much less effective than in the sodium salt, owing to the covalency of the bond S—CH_3. In the first compound, therefore, the C=S bond is much less polar than in the second, and, in agreement with our views, the sulfur of the ester is actually found to undergo exchange much more slowly than the sodium salt. As would be expected, zinc diethyldithiocarbamate occupies an intermediate position with respect to the rate of sulfur exchange.

We observed similar regularities in a study of hydrogen-isotope exchange in the methyl group of salts and derivatives of acetic acid in the presence of heavy acetic acid CH_3COOD[18].

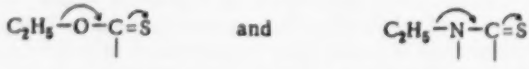
It was found that potassium acetate, which is a stronger base and has a higher negative charge on its oxygen atoms than lead acetate or ethyl acetate, is more effective in the elimination of a proton from the C—H bonds of acetic acid. With respect to hydrogen exchange, these compounds fall into a series similar to the series III:

$$CH_3COOK > (CH_3COO)_2Pb > CH_3COOC_2H_5.$$

The effect of the increase of the polarity of the C=S bond resulting from σ–π-conjugation explains the slower exchange of sulfur in 3-methylthiazolinethione, compared with 2-mercaptobenzothiazole (Series IV):

(1) (2)

We consider that the sulfur of an ethylxanthate salt undergoes exchange more rapidly than that of a diethyldithiocarbamate salt (Series I) for the same reason: the bond O—C_2H_5 is more polar than the bond N—C_2H_5, and the conjugation of these bonds with the bond C=S:



gives rise to a greater negative charge on the sulfur atom in the first case than in the second.

In agreement with these considerations, ethylxanthic acid ($K = 2.8 \cdot 10^{-2}$)

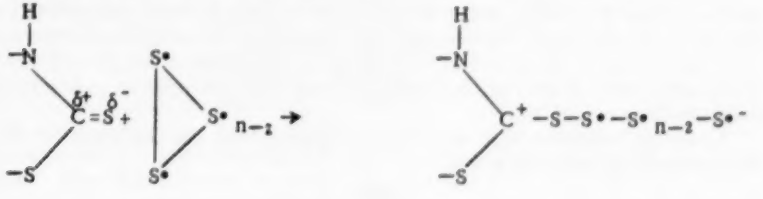
is found to be weaker than diethyldithiocarbamic acid[19] ($K = 4.2 \cdot 10^{-2}$). Hence, the negative charge on the sulfur of the dithio acid grouping is greater in the first acid than in the second.

Similar considerations provide an explanation also for the regularities found in Series V. Here again replacement of the oxygen in the ring by nitrogen reduces the mobility of the sulfur atom lying outside the ring.

We have found recently that, in acetic acid and pyridine solutions, phenylthiourea exchanges its sulfur for elementary sulfur much more rapidly than in toluene and alcohol-toluene solutions. Moreover, addition of a small amount of benzoyl peroxide—a widely used initiator for radical processes—or benzoquinone or diphenylamine—which are radical acceptors—does not affect, or only slightly increases, the rate at which exchange occurs.

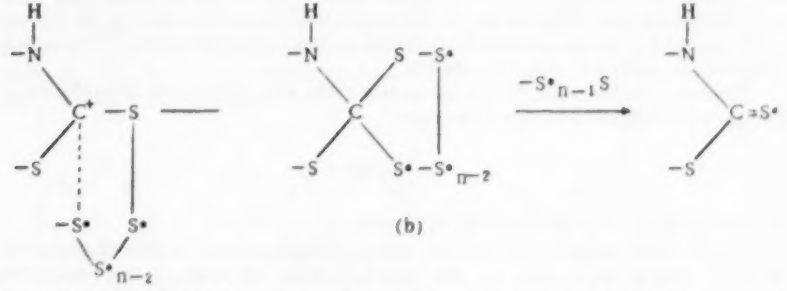
All the data considered above—the effect of bond polarity on the mobility of sulfur, the increased rate of the exchange in presence of acids or bases, and, finally, the absence of any change in the rate of the exchange when initiators or inhibitors of radical processes are added—all these taken together indicate that exchange reactions of sulfur in organic compounds proceed by a heterolytic mechanism.

We assume that the sulfur atoms of cyclic molecules of free sulfur are linked by readily polarizable bonds[20]. In a collision with molecules of a compound in which a sulfur or carbon carries an appreciable negative or positive charge, heterolytic rupture of the bonds between sulfur atoms occurs and an intermediate compound of the type (a) is formed:



(a)

The formation of such compounds is possible also in reactions with thiols, but only in cases similar to the above does the presence of positive charge on the carbon atom result in the conversion of the intermediate compound (a) into the cyclic compound (b):

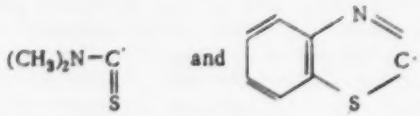


(b)

in which the labeled and normal sulfurs are arranged symmetrically with respect to the remaining part of the molecule. In the thio acids and their salts, ex-

change reactions proceed by the same general mechanism. Both sulfur atoms, of course, take part in the exchange reaction.

On the other hand, in a diethyldithiocarbamic ester, only one sulfur can undergo exchange. This indicates that, under the conditions of the exchange reactions, the bond C—S(CH_3) is not broken. In exactly the same way, according to Syrkin, the bond C—S—S—C in disulfides is also not broken[1]. Hence, the assumption made by Guryanova[21] relating to the rupture of this sort of C—S bond in thiuram and 2-mercaptobenzothiazole, with formation of the radicals:

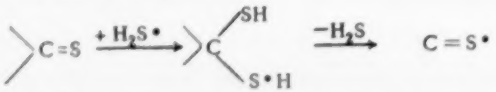


does not appear very likely.

In a study of exchange reactions between free sulfur and the sulfur of derivatives of phosphorodithioic acid, we (L. V. Sulima) discovered some new facts that confirm the proposed mechanism. It was shown that none of the following—*O,O*-diethyl hydrogen phosphorodithioate, sodium *O,O*-diethyl phosphorodithioate, *O,O,S*-triethyl phosphorodithioate, *O,O,O*-tributyl phosphorothioate, and other similar compounds—would enter into exchange reactions with sulfur, even under comparatively severe conditions (100° for several hours)[22].

We consider that, in this case also, the first stage of the exchange reaction—the formation of a compound of the type (a)—occurs, but the subsequent ring closure by the chain of sulfur atoms, with formation of a compound of the type (b), does not occur, because the phosphorus in the dithio acids, as in the usual phosphoric acids, is quadrivalent-positive and does not tend to pass into the quinquevalent condition.

Exchange reactions with hydrogen sulfide proceed via the addition of an H_2S molecule at a double bond:



In aqueous alkaline solutions at 100°, no exchange occurs between 2-mercaptobenzothiazole and hydrogen sulfide. In toluene solution, exchange occurs with measurable speed at 150°. The fact that the exchange of sulfur of 2-mercaptobenzothiazole with sulfur of hydrogen sulfide occurs just as slowly as exchange with free sulfur must be ascribed to the very low degree of ionization of hydrogen sulfide in toluene solution.

The rate constants for the exchange reactions were calculated from the usual kinetic equation for isotopic exchange:

$$k' = -\frac{1}{t} \ln (1 - z)$$

in which z is the fraction exchanged in time t.

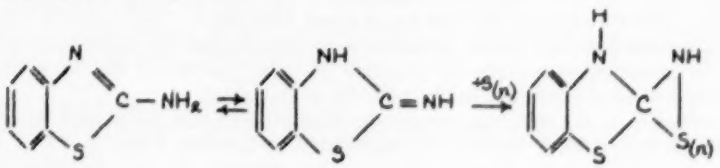
For the usual bimolecular isotopic-exchange reactions, k' is only an apparent constant, being dependent on the concentrations of both of the reactants. When, however, the slowest stage of the exchange is associated with some unimolecular transformation of one of the components, k' is a true first-order constant.

It is interesting that, for exchange reactions in the systems (potassium ethylxanthate + sulfur) and (sodium diethyldithiocarbamate + sulfur), the value of k' does not depend on the concentrations of the reactants, so that these reactions proceed as if they were unimolecular. In the case of 2-mercaptobenzothiazole there is a definite dependence of k' on the concentration of reactants, but the relevant calculation indicates not a second-order, but a fractional-order reaction. According to Guryanova's results[21] k' for the exchange of the sulfur of 2-mercaptobenzothiazole with elementary sulfur depends on the 2-mercaptobenzothiazole concentration, but not on the concentration of elementary sulfur. As in many other cases, these kinetic data may be compatible with several hypotheses concerning the mechanism of the exchange reactions.

The second main conclusion from all of the data examined above is that, in the majority of cases, compounds having the most mobile sulfur atoms are at the same time also the most effective accelerators for the vulcanization of rubber. Thus, in presence of potassium xanthate, the vulcanization of rubber occurs at room temperature, dithiocarbamates are accelerators for vulcanization under mild conditions, 2-mercaptobenzothiazole is a typical accelerator for hot vulcanization, etc. The mobility of sulfur in these compounds falls in the same order. The same effect is indicated by a comparison of the accelerating powers of the compounds of the first series: 2-mercaptobenzothiazole is a typical accelerator, but the oxazole derivative is not very effective; the imidazole derivative is an antioxidant and is not used at all as an accelerator.

An investigation by Bresler[22] of the kinetics of exchange and of vulcanization for the case of thiuram showed that they are very similar. On the other hand, according to Dogadkin's results[23], the exchange and accelerator reactions of 2-mercaptobenzothiazole, proceed at different rates. These contradictory results may be explained as follows. It is logical to suppose that vulcanization is produced by sulfur that is splitting stepwise from an intermediate compound of type (b). The splitting of the —S—S—S— bonds apparently occurs homolytically, and separate sulfur atoms or fragments (containing 2, 3, etc., atoms) enter the solution and bring about the vulcanization of the rubber. This process must be a rapid one, like the breakdown of trisulfides into disulfides and sulfur[1]. For the exchange, however, the breaking of C—S bonds must occur, and this will occur with a much higher activation energy. This can explain the difference in the rates of vulcanization and of exchange. In those cases in which the intermediate compound (b) breaks down the rupture of C—S bonds, exchange will occur at the same rate as vulcanization.

Finally, let us consider compounds that do not contain sulfur but accelerate vulcanization. It must be supposed that such compounds either react chemically with sulfur under vulcanization conditions with formation of sulfur-containing thiones or thio acids, or are able to form intermediate compounds with sulfur of type (c), analogous in structure to compounds of type (b). For example, the feeble accelerator, 2-aminobenzothiazole, may form the cyclic compound (c) with sulfur:



(c)

and the stepwise decomposition of this will yield atoms or groups of atoms of sulfur in the solution, which will cause vulcanization.

There are some data, however, which are not in accord with the hypothesis of the common origin of the acceleration and exchange processes. For example, elementary sulfur does not undergo exchange with the sulfur of 2-mercaptobenzothiazole in presence of zinc oxide[24], although the latter is always added to rubber and does not hinder vulcanization. The absence of exchange has a simple explanation: the zinc mercaptide has the thiol structure, and there is no C=S group containing sulfur capable of undergoing exchange. The role of zinc oxide in vulcanization is not clear. It is possible that it neutralizes the acid components of the rubber and that 2-mercaptobenzothiazole is already present in the form of the thione tautomer in the mixture undergoing vulcanization.

It will be clear from this discussion that the investigation of the exchange reactions of sulfur in organic compounds is of great importance for the elucidation of a number of problems in sulfur chemistry and, in particular, for the establishment of the mutual effects of atoms and the effect of σ–π-conjugation on the mobility and reactivity of sulfur in various compounds. At the same time, these studies are closely associated with the mechanism of the action of accelerators in the vulcanization of rubber, and provide material for the discovery of methods for their selection and use.

SUMMARY

The paper presents the results of investigations of the mobility of bivalent sulfur in organic compounds having C—SH, C—SC, CS—SC, C—S and

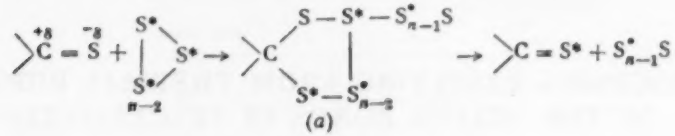
bonds, obtained by studying the exchange reactions of corresponding compounds with radioactive sulfur.

Particular attention is devoted to isotope exchange of sulfur and hydrogen sulfide with sulfur-containing organic compounds used as accelerators of rubber vulcanization. Verification and ascertainment of the nature of the interaction between the sulfur in molecules of rubber vulcanization accelerators, and free sulfur may be of help in understanding the mechanism of action of rubber vulcanization accelerators which remains unknown.

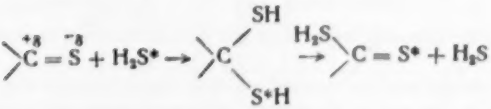
The data of such an investigation are of value, for the chemistry of organic sulfur compounds has been studied too little. Examination of the results, obtained by the authors and other investigators, shows that the sulfur in the C—SH, C—S and CS—SC bonds of organic compounds has little mobility and interchange either with free sulfur or with H_2S even under relatively strenuous conditions. On the contrary, the sulfur of the thione group C=S and the central sulfur atom of trisulfides are of great mobility.

The data obtained can be explained if we assume that the mobility of sulfur in the investigated compounds depends on polar factors for the X=S bonds increases with the increase of the polarity of the latter.

In this case, the exchange mechanism of organic thione compounds with free sulfur or the sulfur of H_2S can be represented by schemes I and II.



(a)



The majority of compounds having more labile sulfur atoms are at the same time more effective rubber vulcanization accelerators.

However this parallelism has many exceptions.

In a number of cases the rate of vulcanization greatly surpasses the rate of isotope exchange. It may be supposed that sulfur activation by an accelerator is connected with the formation of an intermediate compound capable of gradually splitting the atoms (or groups of atoms) of sulfur as the latter pass into the reactive medium and perform vulcanization. The formation of such active splinters may originate only by the rupture of S—S but not C—S bonds while to realize an exchange the rupture of more hard bonds between sulfur and carbon is required.

All this may explain the considerably lower rate of sulfur isotope exchange in 2-mercaptobenzothiazole, as compared to the rate of vulcanization in presence of this accelerator.

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$$S^{--} + S_n^{-} - - - - - S^{-} \rightarrow n\,S_n$$

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PROCESSES RESULTING FROM THERMAL RUPTURE OF THE SULFUR BONDS IN VULCANIZATES *

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In earlier works[1] we had studied in detail the rupture of the molecular chains of rubber under the action of oxygen, high temperatures, mechanical stresses, and some other factors. V. A. Kargin and G. L. Slonimskiĭ have directed our attention also to the possibility of a thermal rupture of the polysulfide sulfur bonds which form the structural network of vulcanizates. Dogadkin and Tarasova[2] observed a rupture of the polysulfide bonds in vulcanizates under the action of mechanical stresses at temperatures of 100° and 130° C, and also on dissolving the vulcanizates in Synthol (motor oil) at 180–190°. All the experiments were carried out by the authors in the absence of oxygen.

There are no indications to be found in the literature as to the behavior of the free radicals which are formed as a result of the rupture of sulfur bonds. The present work is devoted to an exploration of this important question.

The experiments[3] were performed with vulcanizates of three types: (1) monosulfide (mainly intermolecular bonds of the type, —C—S—C); (2) polysulfide (mainly intermolecular bonds of the type, —C—S_n—C—); (3) heat-vulcanizate (—C—C— bonds). Vulcanizing conditions were chosen such that the several vulcanizates would have approximately the same equilibrium modulus.

The monosulfide vulcanizate was obtained with this recipe: 100 parts rubber by weight, 1.0 part phenyl-2-naphthylamine, 2.0 parts stearic acid, 5.0 parts zinc oxide and 3.0 parts tetramethylthiuram disulfide. Vulcanization was at 143° C for 90 minutes.

The polysulfide vulcanizate was obtained with this recipe: 100 rubber, 1 phenyl-2-naphthylamine, 2 stearic acid, 5 zinc oxide, 6 sulfur and 1 diphenylguanidine. Vulcanization was at 143° C for 20 minutes.

The heat-vulcanizate was obtained with the recipe: 100 rubber, 2 stearic acid, 1 phenyl-2-naphthylamine. Vulcanization was at 220° C for 60 minutes.

Sodium-catalyzed polybutadiene (sodium-butadiene) rubber was the base material from which all the vulcanizates were prepared. All antioxidants, free sulfur, accelerators, and their decomposition products were completely removed by extraction for 50 hours in the cold with acetone, in an atmosphere of nitrogen. In some experiments, the antioxidant and sulfur were introduced into the extracted vulcanizate through swelling in xylene solutions. The vulcanizates were tested in the form of thin strips with a thickness of 180–200μ. The study of the oxidation of the vulcanizates and the consumption of the antioxidant in this process was carried out by methods which were described earlier[4].

In previous communications it was pointed out that free sulfur dissolved in rubber acts as an antioxidant for the rubber. In Figure 1 are presented curves of oxidation of a heat-vulcanizate (*1*), a polysulfide vulcanizate (*2*), and a heat-vulcanizate containing free sulfur (*3*). (None of these three vulcanizates con-

* Translated for Rubber Chemistry and Technology by Malcolm Anderson from *Doklady Akademii Nauk SSSR*, Vol. 90, No. 3, pages 409–412 (1953).

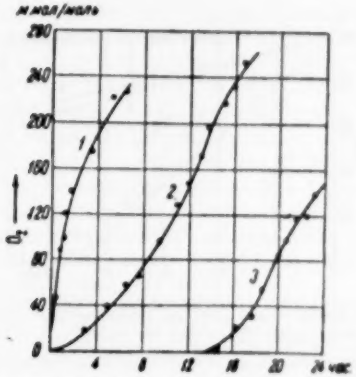

FIG. 1.—Kinetics of vulcanizate oxidation at 130° C. *1*—Heat-vulcanizate. *2*—Sulfur vulcanizate without free sulfur (3% combined sulfur, mainly polysulfide sulfur). *3*—Heat-vulcanizate with free sulfur (3% sulfur introduced by means of swelling). The abscissa represents time of oxidation in hours; the ordinate the amount of oxygen absorbed in millimoles/mole.

tained phenyl-2-naphthylamine.) As can be seen, not only free sulfur but also combined polysulfide sulfur have distinct inhibiting properties. Actually, the rate of oxidation is 15 to 20 times less in a polysulfide vulcanizate than in a heat-vulcanizate.

In the thermal rupture of the polysulfide bonds, for example, according to the equation:

$$\text{—C—S—S}_n\text{—S—C—} \longrightarrow \text{—S}_n\text{—} + 2\,\text{—C—S—},$$

the $\text{—S}_n\text{—}$ radicals which are formed recombine with the radicals of the oxidizing chains, giving an inhibiting effect.

In another series of experiments, the influence of polysulfide sulfur on the rate of consumption of phenyl-2-naphthylamine in the oxidation of vulcanizates (Figure 2) was investigated. It is known that free sulfur inhibits the consumption of phenyl-2-naphthylamine (segment Ab of curve *2*). Molecules of free sulfur combine with the peroxide radicals of the rubber to produce new radicals of low reactivity, which are unable to detach the hydrogen atom from the anti-

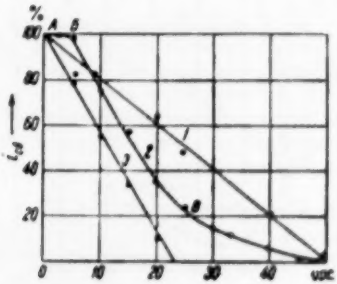

FIG. 2.—The influence of free sulfur on the kinetics of phenyl-2-naphthylamine consumption. Oxidation temperature, 130° C. *1*—Heat-vulcanizate. *2*—Vulcanizate with 0.155% free sulfur (3% total sulfur). *3*—Vulcanizate with 3% combined sulfur (mainly polysulfide). The abscissa represents the time of oxidation in hours; the ordinate (i_{CA}) the percentage of free phenyl-2-naphthylamine.

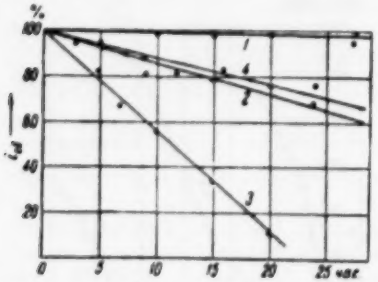

FIG. 3.—Kinetics of phenyl-2-naphthylamine consumption in vulcanizates with different types of cross-links. Oxidation temperature, 130° C. *1*—Vulcanizate containing mainly polysulfide sulfur (in nitrogen). *2*—Vulcanizate containing mainly monosulfide sulfur (in oxygen). *3*—Vulcanizate containing mainly polysulfide sulfur (in oxygen). *4*—Heat-vulcanizate (in oxygen). The abscissa represents the time of oxidation in hours; the ordinate the percentage of free phenyl-2-naphthylamine.

oxidant molecule, and hence paralyze the action of the antioxidant. As a result of this, the antioxidant is no longer being consumed, and in its presence an intense autocatalytic process develops[6].

An entirely different picture is seen in vulcanizates containing combined polysulfide sulfur (segment bB of curve *2* and the straight line *3*). In the process of oxidation in such vulcanizates, the rate of antioxidant consumption considerably exceeds the rate of its consumption in the heat-vulcanizate (straight line *1*).

One might suppose that the free radicals, formed when the polysulfide bonds in the vulcanizate decompose, react with the antioxidant and consequently bring about an increase of its rate of consumption, in comparison with that in the heat-vulcanizate. If such an assumption is correct, then when a polysulfide vulcanizate is heated in nitrogen, some consumption of antioxidant should occur.

Experiments which we set up specially (straight line *1* in Figure 3) showed that there is no consumption of antioxidant in nitrogen. Consequently, the

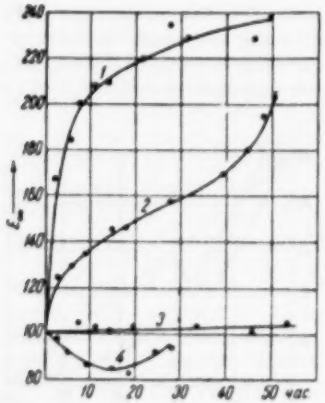

FIG. 4.—Kinetics of the change in the high-elasticity equilibrium modulus when the vulcanizates are heated in various media. *1* and *2*—Vulcanizate containing mainly polysulfide sulfur (*1*—in nitrogen; *2*—in oxygen). *3* and *4*—Vulcanizate containing mainly monosulfide sulfur (*3*—in nitrogen; *4*—in oxygen). The abscissa represents time of heating in hours; the ordinate the modulus (E_∞) in percentage of the initial modulus.

radicals which form during the thermal decomposition of polysulfide bonds are of low activity in the reaction with the antioxidant. It is evident that the increase of the rate of antioxidant consumption results from its reaction with the radicals which are formed when the decomposition products of the polysulfide sulfur react with oxygen or with the oxidation products of rubber.

We shall not go at present into a discussion of the mechanism of the reaction between the antioxidant and the active centers in the vulcanizate. We shall only call attention to the exceedingly interesting fact that the products formed when free sulfur combines with the vulcanizate under oxidation, and those formed when its polysulfide bonds are ruptured, behave in two different ways toward the antioxidant. The former decrease the rate of antioxidant consumption, whereas the latter increase it.

Figure 3 presents straight lines representing the consumption of the antioxidant in the process of oxidation of polysulfide and monosulfide vulcanizates (lines *2* and *3*) and of a heat-vulcanizate (line *4*). As can be seen, monosulfide bonds have no influence on the speed of the inhibited oxidation of the vulcanizate. Evidently the monosulfide bonds are quite stable at 130° C.

In Figure 4 are presented curves of the change of the equilibrium moduli of polysulfide and monosulfide vulcanizates under a process of heating in different media. As one would expect, the rate of structural changes in the polysulfide vulcanizate is considerably greater than that in the monosulfide vulcanizate.

It is interesting that, under oxidation, even a different type of structural change is observed. In the polysulfide vulcanizate the modulus rises, whereas in the monosulfide it falls. Although the structure of the monosulfide vulcanizate changes hardly at all during heating in nitrogen, in the polysulfide vulcanizate considerable structure formation is noted with heating. A sharp increase of the number of cross-links during the heating of the polysulfide vulcanizate in nitrogen indicates without a doubt the simultaneous progress of reactions of rupture and those forming new sulfide cross-links of a lower order.

We have established that oxidative destruction in all rubbers, regardless of their structure, is accompanied by polymerization reactions. Taking into account the new data, we may consider it established that the operation of simultaneous destructive and structure forming reactions is the general rule for reactions in polymers built up with the help of free radicals. The lower rate of structure formation of the polysulfide vulcanizate in oxygen, compared with that in nitrogen, is the result of the superimposed oxygen destruction.

The results obtained by us relate only to vulcanizates not under a condition of stress.

As we have shown[6], when a vulcanizate is subjected to an elongation stress, this sharply changes the ratio between destruction and structure formation.

The general conclusion which may be drawn from the present work is that the polysulfide bonds in a vulcanizate lower its chemical stability toward oxygen. By the thermal rupture of polysulfide bonds, free radicals are generated, and these are the source of the initiation of various processes in vulcanizates.

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SULFUR EXCHANGE IN POLYSULFIDES AND IN VARIOUS VULCANIZATION ACCELERATORS *

E. N. Guryanova, V. N. Vasilyeva, and L. S. Kuzina

The establishment of the relation between structure and reactivity is one of the basic problems of modern organic chemistry. The greatest discovery of man—the utilization of atomic energy—provided chemistry with a new, powerful method for the study and solution of this problem, namely, the method of labeled atoms.

The application of this method to the investigation of the relation between the reactivity of a substance and its molecular structure has proved to be very promising and has already given important results, particularly with respect to the reactivity of hydrogen in various compounds.

With the aid of this tracer method, much information has been obtained about the mobility of halogen atoms in organic compounds. As regards sulfur compounds, these have received little investigation of this sort until recently. The organic compounds of sulfur, however, occur extensively among natural substances and find various applications in chemical practice, so that the establishment of the laws governing the mobility of sulfur atoms as a function of molecular structure is extremely important. This problem can be solved by the use of the radioactive isotope S^{35}.

It can be expected that the investigation of exchange reactions with elementary sulfur will enable us also to elucidate the mechanism of the separation of a sulfur atom from the S_8 molecule. Moreover, the investigation of exchange reactions has an interest for its own sake, as the simplest method for the synthesis of labeled sulfur-containing compounds.

In the present investigation we have used the isotopic-exchange method for the investigation of the effect of molecular structure on the exchange propensity of sulfur atoms in the bonds S—S, C—S, and C=S in organic polysulfides and in certain compounds that can act as vulcanization accelerators.

We shall not discuss the experimental procedure used—the synthesis and purification of the preparations and the methods of separating the components of the mixture obtained from the exchange reaction (a matter of special importance in work with radioactive tracers)—we shall merely indicate that in all cases the distribution of the radioactive isotope between the components of the reaction mixture was determined by drawing up a full balance sheet of the activity, the sulfur of any compound being converted into SO_4'' and the activity of the sample determined in the form of a precipitate of benzidine sulfate.

EFFECT OF THE RADICAL ON THE MOBILITY OF SULFUR IN ORGANIC POLYSULFIDES

In a study of organic polysulfides of the type R—S—S—S—R, we found that the middle sulfur atom undergoes exchange fairly readily with radioactive

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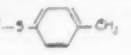
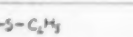
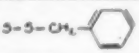
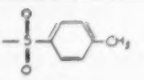
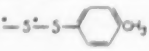
elementary sulfur, with formation of labeled compounds of the type R—S—S*—S—R. The middle sulfur atoms of a polysulfide bridge are also able to undergo exchange with the middle sulfurs of another polysulfide. For example, if we treat ditolyl trisulfide, $CH_3C_6H_4$—S—S*—S—$C_6H_4CH_3$, and then distil off the diethyl trisulfide in a vacuum, the distillate is radioactive. In the diethyl trisulfide so obtained, only the middle sulfur atom is active, C_2H_5—S—S*—S—C_2H_5.

We have observed similar exchange reactions in other systems; they have been observed also in vulcanized rubbers[1]. The question arises of the mechanism of the exchange of sulfur atoms between polysulfides.

TABLE 1

EXCHANGE OF SULFUR BETWEEN POLYSULFIDES AND ELEMENTARY RADIOACTIVE SULFUR

System	Structural formula of product	Temperature, ° C	k·10⁴	E (kcal/mole)
Tolyl trisulfide + S_8* in xylene (0.14 N)	 (See note below)	80 92 102 126	0.85 1.42 2.45 10.32	14.5
Ethyl trisulfide + S_8* in xylene (0.31 N)	 (See note below)	129.3 140 149.5 166	1.25 3.1 6.1 19.1	27.3
Benzyl trisulfide + S_8*	 No exchange	130 (5 hours)	—	—
4-Tolylsulfonyl sulfide + S_8*	 No exchange	140 (20 hours)	—	—
4-Tolyl tetrasulfide + S_8*		80 (10 hours)	—	—

* Note: Also polysulfides containing a greater number of sulfur atoms.

This reaction could be brought about in two ways: either the exchange is effected by the transfer of a sulfur atom from one polysulfide to the other, which must occur with the rupture of four S—S bonds, or the polysulfides exchange RS—groups. After carrying out special experiments, including some with a labeled R radical, we convinced ouselves of the correctness of the second supposition[2]. When heated and irradiated with ultraviolet radiation, polysulfides break down at the S—S bonds, with formation of RS—, RSS*—, and other groups, the recombination of which results in the appearance of the labeled sulfur atom in a molecule that did not originally contain one.

The first, purely quantitative experiments on sulfur exchange in polysulfides showed that the mobility of sulfur atoms in polysulfide linkages depends greatly on the nature and structure of the radical[3].

In order to determine the effect of the radical on the mobility of sulfur atoms in polysulfide bridges, we measured the rate of sulfur exchange between organic trisulfides and radioactive elementary sulfur in solutions at various temperatures. The course of the reaction was followed by the reduction in the activity of the elementary sulfur.

Table 1 gives a summary of the results: k is the rate constant for isotopic exchange, calculated from the formula

$$k = -\frac{2.3}{t}\log\left[\left(\frac{a}{b}+1\right)\frac{x}{x_0}-\frac{a}{b}\right],$$

in which x is the activity of the sulfur at time t, x_0 is the initial activity of the sulfur, and a and b are the concentrations of trisulfide and sulfur, respectively; E is the activation energy, determined from the experimentally found relation between k and $1/T$.

A comparison of the results will show the great difference in the behavior of the middle sulfur atoms in polysulfides having aliphatic and aromatic radicals. The activation energy for the exchange reaction with tolyl trisulfide is 14.5 kcal./mole, whereas the value for the reaction with diethyl trisulfide is 27.3 kcal./mole. The effect of the radical on the behavior of sulfur in a polysulfide bridge is clearly seen also in benzyl trisulfide and 4-tolylsulfonyl sulfide.

Purely quantitative experiments on the exchange of sulfur in tolyl tetrasulfide show that the exchange of the middle sulfur atoms in this compound proceeds approximately in the same way as in tolyl trisulfide. In further work we propose to determine the way in which the character of the sulfur linkages in polysulfides varies with increase in the number of sulfur atoms (tri-, tetra-, hexasulfides). The reaction of S exchange between polysulfides and elementary sulfur is accompanied by side reactions in which sulfur is incorporated into the polysulfide bridge, with formation of polysulfides having more sulfur atoms than the original compounds. This leads to difficulties in the investigation of the reaction mechanism.

In order to determine the effect of the radical on the behavior of S—S bonds in organic disulfides, we studied the exchange of RS—groups between disulfides and the corresponding thiols:

$$RS^*—S^*R + RSH \longrightarrow RS^*H + RS—S^*R.$$

The course of the reaction was followed by observation of the appearance of radioactive sulfur atoms in the thiol molecule RS*H. Experiments on the kinetics of the exchange of RS— groups between disulfides and thiols were carried out in hydrocarbon solution at different temperatures. The results are given in Table 2. In the fourth column of the table, values of k, the apparent rate constant for the exchange, are given; they were calculated from the formula:

$$k = -\frac{2.3}{t}\log\left(1-\frac{x}{x_\infty}\right)$$

in which x is the activity of thiol at time t, and x_∞ is its activity at equilibrium.

The fifth column gives the values of k at 100°, which were obtained by extrapolation of the experimental values of k. The sixth gives k_x/k_{P_A} (at 100°), in which k_x is the apparent rate constant for exchange in any of the investigated systems at 100°, and k_{P_A} is the apparent rate constant for exchange in the

TABLE 2

EXCHANGE OF RS—GROUPS BETWEEN DISULFIDES AND THIOLS: RS*—S*R + RSH ⇌ RS*H + RS—S*R

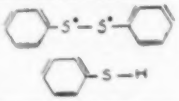
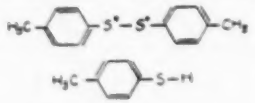
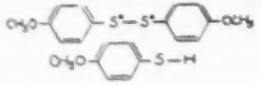
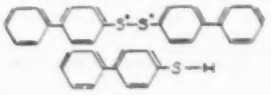
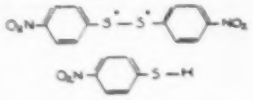
System	Structural formulas of reactants	Temperature (° C)	$k \cdot 10^4$	$k \cdot 10^4$ at 100°	$\frac{k_x}{k_{PhS}}$ (100°)	E (kcal./mole)
Phenyl disulfide + benzenethiol in benzene (C_d = 0.1 N; C_t = 0.1 N) [See note below]		35	0.20			
		41	0.37			
		61.5	0.83			
		79	1.67	3.5	1	10
Tolyl disulfide + *p*-toluenethiol in xylene (C_d = 0.1 N; C_t = 0.1 N)		77	0.4			
		95	0.9			
		102	1.2			
		120	3.2			
		129	5.1			
		142	6.6	1.3	0.37	13
Bis(methoxyphenyl)disulfide + *p*-anisolethiol in xylene (C_d = 0.1 N; C_t = 0.1 N)		101	0.4			
		119.5	1.6			
		144.5	3.6			
		164	8.9	0.5	0.14	14.4
4-Biphenyl disulfide + 4-biphenylthiol in xylene (C_d = 0.1 N; C_t = 0.1 N)		110	0.5			
		138	21.			
		160	4.7	0.3	0.09	14.4
4-Nitrophenyl disulfide + 4-nitrobenzenethiol in xylene (C_d = 0.1 N; C_t = 0.1 N)		104.5	0.27			
		116.5	0.63			
		126.5	1.5			
		142.5	4.8			
		145	5.3	0.18	0.05	23

TABLE 2 (continued)

System	Structural formulas of reactants	Temperature (° C)	$k \cdot 10^4$	$k \cdot 10^4$ at 100°	$\frac{k_T}{k_{T_0}}$ (100°)	E (kcal./mole)
Butyl disulfide + 1-butanethiol in decahydronaphthalene (C_d = 0.5 N; C_t = 0.5 N)	$C_4H_9-\dot{S}-\dot{S}-C_4H_9$ C_4H_9-S-H	169 193 195 213 231	0.1 0.7 0.8 2.4 7.3	$1.6 \cdot 10^{-4}$	$4.6 \cdot 10^{-5}$	28
Benzyl disulfide + α-toluenethiol in decahydronaphthalene (C_d = 0.5 N; C_t = 0.5 N)	$C_6H_5-CH_2-\dot{S}-\dot{S}-CH_2-C_6H_5$ $C_6H_5-CH_2-S-H$	182 192 202 228	0.4 0.67 1.6 8.8	$9 \cdot 10^{-5}$	$2.5 \cdot 10^{-5}$	31
Phenyl disulfide + 1-butanethiol in xylene (C_d = 0.1 N; C_t = 0.1 N)	$C_6H_5-\dot{S}-\dot{S}-C_6H_5$ C_4H_9-S-H	41 50.5 60 69.5	0.6 0.8 1.6 2.5	0.4	1	10
Butyl disulfide + benzenethiol in xylene (C_d = 0.5 N; C_t = 0.5 N)	$C_4H_9-\dot{S}-\dot{S}-C_4H_9$ C_6H_5-S-H	197 214.5 227 235	1.2 2.7 7.1 7.9	$2 \cdot 10^{-4}$	$6 \cdot 10^{-5}$	27.4

Note: C_d is concentration of disulfide; C_t is concentration of thiol.

TABLE 3

Butyl disulfide +1-butanethiol in decahydronaphthalene; 196° ±1° C				*p*-Tolyl disulfide +*p*-toluenethiol in xylene; 120° ±0.5° C				Benzyl disulfide +α-toluenethiol in decahydronaphthalene; 202° +1° C			
C_t	C_d	$k \cdot 10^4$	$k \cdot 10^3$	C_t	C_d	$k \cdot 10^4$	$k \cdot 10^3$	C_t	C_d	$k \cdot 10^4$	$k \cdot 10^3$
0.25	0.5	1.1	0.15	0.05	0.1	4.5	1.4	0.25	0.5	1.0	0.14
0.5	0.5	1.0	0.14	0.1	0.1	3.8	1.2	0.5	0.5	1.3	0.18
5.0	0.5	0.9	0.13	0.3	0.1	4.0	1.3	1.0	0.5	1.1	0.16
0.5	0.25	0.8	0.16	0.1	0.05	2.6	1.2	2.5	0.5	1.1	0.16
0.5	0.5	1.0	0.14	0.1	0.1	3.8	1.2	0.5	0.5	1.3	0.18
0.5	2.5	1.9	0.13	0.1	0.5	9.3	1.3	0.5	1.0	1.7	0.17
								0.5	2.5	3.2	0.20

system, phenyl disulfide + benzenethiol at 100°. Finally, the seventh column gives values of the activation energy for the exchange reaction.

It will be seen from the data in Table 2 that the conditions for the exchange of RS— groups between disulfides and thiols vary greatly from one system to another. For example, exchange of RS— groups between phenyl disulfide and benzenethiol proceeds at an appreciable rate at only 35°, whereas exchange between *p*-nitrophenyl disulfide and *p*-nitrobenzenethiol goes at about the same rate only at 100–105°. Exchange is still more difficult in systems of compounds containing aliphatic and benzyl radicals. This is particularly obvious when reaction rates and activation energies are compared.

What is the cause of such a great variation in the conditions required for the exchange of RS— groups between the disulfides and thiols investigated? In order to answer this question it is essential to know the mechanism of the exchange reactions. With this object we measured reaction rates at various concentrations of reactants[4], the concentration of one component being varied

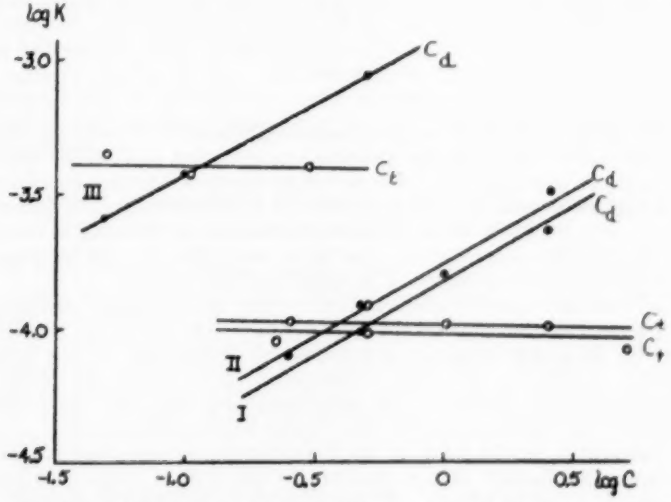


FIG. 1.—Dependence of the rate of the exchange reaction on the concentration of reactants. I) Butyl disulfide + 1-butanethiol; II) benzyl disulfide + α-toluenethiol; III) p-tolyl disulfide + *p*-toluenethiol.

while that of the other remained constant. The results of these experiments are given in Table 3.

The first column gives the concentration of thiol C_t (mole/liter), the second gives the concentration of disulfide C_d (mole/liter), and the third gives values of

$$k = (C_d \cdot C_t) = -\frac{2.3}{t} \log \left(1 - \frac{x}{x_\infty}\right)$$

It will be seen from the table that, in all three systems, a ten-to-twenty-fold increase in the concentration of thiol has practically no effect on the apparent rate constant for the exchange. However, change of the concentration of the disulfide at constant concentration of thiol results in a considerable change of the value of k. The dependence of k on the concentration of reactants is seen more clearly when represented graphically; in Figure 1 the data of Table 3 are represented in the form of graphs.

It will be seen from the courses taken by the lines that in all three systems the rate of exchange of RS— groups between disulfides and thiols is independent of the thiol concentration and is proportional to the square root of the disulfide concentration. Hence, $k = k'\sqrt{C_d}$, or $k' = \frac{k}{\sqrt{C_d}}$. Values of k' calculated from this formula are given in the fourth column of Table 3 and, as will be seen, its constancy is maintained quite satisfactorily for all values of C_d and C_t. Hence, on the basis of the results obtained for the three systems investigated, it may be considered that the exchange of RS— groups between disulfides and thiols is not a simple bimolecular reaction in which there is a collision between the molecules RS*—S*R and R—S—H accompanied by a rearrangement of bonds:

If the exchange reaction occurred in accordance with this scheme, then the rate would depend both on the disulfide concentration and on the thiol concentration. It is evident that the exchange reaction between disulfides and thiols is a more complex process and proceeds in several stages. The fact that the rate is independent of the thiol concentration and proportional to the square root of the disulfide concentration may be an indication that the limiting stage is the process of the breakdown of the disulfide into radicals.

The hypothesis that the reactions that we have studied have a radical mechanism is confirmed, not only by the kinetic results, but also by the fact that the reaction of RS-group exchange is considerably accelerated by the action of ultraviolet radiation[2]. Finally, we succeeded in detecting the presence of radicals in solutions of some of the investigated disulfides by purely chemical methods, i.e., by the reaction with 2,2-diphenyl-1-picryl-hydrazyl.

Consequently, in the light of the experimental results obtained, we may describe the mechanism of the reaction of exchange of RS-groups between disulfides and thiols as follows. Under suitable conditions the disulfide forms $\dot{R}\dot{S}$ radicals. The labeled radical collides with a thiol molecule and removes

its hydrogen atom with formation of a labeled thiol molecule and an unlabeled RS˙ radical. The activity of the sulfide formed as a result of the recombination of RS˙ radicals falls correspondingly. The slowest stage is that of the decomposition of the disulfide into radicals. If this is so, then there should be a direct relationship between the activation energy for the exchange reaction and the ability of the disulfide to break down into radicals at the S—S bond. This conclusion is confirmed experimentally when the kinetics of the exchange of RS-groups between disulfides and thiols having different R radicals are investigated. Table 2 gives data on the exchange between phenyl disulfide and 1-butanethiol, and also between butyl disulfide and benzenethiol, and these show that the rate and activation energy of the exchange reaction do not depend on the identity of the thiol, but are determined solely by the character of the S—S bond in the disulfide. In the future we hope to make a detailed investigation of the mechanism of the exchange reaction which will enable us to relate the activation energy for exchange with the S—S bond energy in disulfides. At present we can make only a quantitative estimation of the effect of the radical R on the strength of the S—S bond in disulfides.

It follows from the data in Table 2 that the introduction of any substituent in aromatic disulfides (CH_3, OCH_3, C_6H_5, NO_2), irrespective of its polarity, has the same effect with respect to sign on the homolytic strength of the S—S bond. In all cases the S—S bond is strengthened, compared with unsubstituted phenyl disulfide. With respect to the magnitudes of their effects, the substituent groups fall into the following order:

$$H < CH_3 < OCH_3 \leqslant C_6H_5 < NO_2$$

An increase of the homolytic strength of an S—S bond as the result of the introduction of substituents, irrespective of their polarity, is probably a general law for the homolytic reactions of substituted aromatic compounds.

Quantum-chemical calculations on bond orders in aromatic compounds indicate that any substituent (irrespective of its polarity) produces an increase of the free-valency index of the *ortho*- and *para*-carbon atoms. The change in the degree of binding of the ortho- and para-carbon atoms under the influence of a substituent of any polarity in the benzene ring probably determines the regularities that we have observed in the behavior of the S—S bond in substituted disulfides.

EFFECT OF MOLECULAR STRUCTURE ON THE MOBILITY OF SULFUR IN C—S AND C=S BONDS

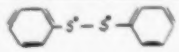
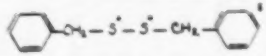
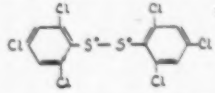
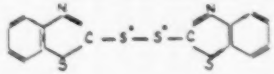
The sulfur in C—S bonds generally undergoes exchange with elementary sulfur much less readily than the sulfur in S—S bonds. In some compounds, however, the difference is small.

Table 4 gives the results of experiments on exchange with radioactive elementary sulfur. The tendency for sulfur attached to carbon to undergo exchange depends greatly on the structure of the molecule: the sulfur of thiocarbamoyl and 2-mercaptobenzothiazole derivatives undergoes exchange with elementary sulfur at 100–130°, whereas the exchange of the sulfur of benzenethiol, butyl disulfide, phenyl disulfide, etc., occurs only at 200–230°. In order to appreciate the significance of these results, it is essential to know the mechanism of the sulfur-exchange reaction undergone by these compounds.

For some of these systems we have investigated the dependence of the rate

TABLE 4

EXCHANGE OF SULFUR IN THE BONDS C—S AND C=S WITH RADIOACTIVE ELEMENTARY SULFUR

No.	System	Structural formula of product	Temperature (° C)	$k \cdot 10^6$	E (kcal/mole)	Extent of exchange (%)
1	2	3	4	5	6	7
1	Phenyl disulfide + S*	 [1]	200 (4 hours)	—	—	0
			230 (4 hours)	—	—	60
2	Benzyl disulfide + S*	 [2]	200 (4 hours)	—	—	~80
3	Butyl disulfide + S*	$C_4H_9-S^*-S^*-C_4H_9$ [3]	200 (4 hours)	—	—	~70
4	2,4,6-Trichlorophenyl disulfide + S* in naphthalene (0.35 *N*)	 [4]	216.5	0.18		
			226.7	0.29		
			252.8	2.88		
			265.7	9.00	47.3	
5	2-Benzothiazolyl disulfide + S* in naphthalene (0.18 *N*)	 [5]	147.3	0.76		
			158	1.34		
			169	2.10		
			178.5	4.18	23	

[1] Exchange is accompanied by the formation of polysulfides having a higher number of sulfur atoms.
[2] Exchange is accompanied by the formation of hydrogen sulfide and polysulfides.
[3] The two middle sulfur atoms most readily undergo exchange.
[4] Exchange is accompanied by the separation of a metal sulfide.
[5] Exchange is accompanied by side reactions and decomposition of the product.
[6] In toluene (0.06 *N*).
[7] In a 30:70 mixture of toluene and alcohol (0.06 *N*).
[8] In a 30:55:15 mixture of toluene, alcohol, and water (0.06 *N*).

TABLE 4 (continued)

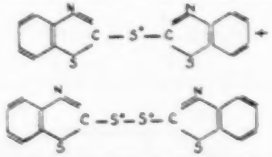
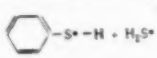
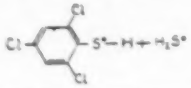
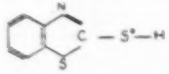
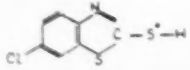
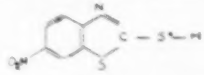
No.	System	Structural formula of product	Temperature (° C)	$k \cdot 10^4$	E (kcal/mole)	Extent of exchange (%)
1	2	3	4	5	6	7
6	2-Benzothiazolyl sulfide + S*		150 (5 hours)	—	—	100
7	Benzenethiol + S*		240 (5 hours)	—	—	100
8	2,4,6-Trichlorobenzenethiol + S*		200 (5 hours)	—	—	50
9	2-Mercaptobenzothiazole + S* (1:1) in naphthalene (0.24 *M*)		131 149 160.4 181.8	0.48 1.57 4.08 14.20	 24	
10	6-Chloro-2-mercaptobenzothiazole + S* (1:1) in naphthalene (0.24 *M*)		128.5 139.7 160.3 172	0.27 0.54 2.58 5.50	 24.2	
11	2-Mercapto-6-nitrobenzothiazole + S* (1:1) in naphthalene (0.06 *M*)		118 134.3 153 160 171	0.07 0.31 1.30 1.54 3.40	 24.9	

TABLE 4 (continued)

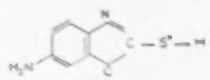
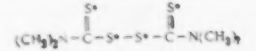
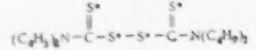
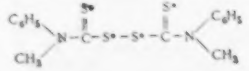
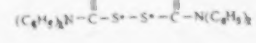
No.	System	Structural formula of product	Temperature (° C)	$k \cdot 10^6$	E (kcal/mole)	Extent of exchange (%)
1	2	3	4	5	6	7
12	6-Amino-2-mercaptobenzothiazole + S* (1:1) in naphthalene (0.1 *M*)		130	—	—	
13	Dimethylthiocarbamoyl disulfide + S* in naphthalene (C_t 0.1 *N*, C_s 0.2 *N*)		110 120 130 136.5 150	0.22 0.42 0.87 1.95 7.10	 21.5	
14	Diisobutylthiocarbamoyl disulfide + S* in benzene (C_t 0.1 *N*, C_s 0.4 *N*)		110.5 120.5 133.5 144 148.5	0.46 1.03 2.50 6.0 7.8	 24	
15	Methylphenylthiocarbamoyl disulfide + S* in xylene (C_t 0.1 *N*, C_s 0.4 *N*)		131 138 141 150	0.6 1.0 1.46 2.6	 26.7	
15a	Diphenylthiocarbamoyl disulfide + S* in toluene (C_t 0.015 *N*, C_s 0.03 *N*)		132.5 146 168.5	0.6 1.8 9.9	 27.8	
16	Diisopropyl dixanthate + S* in naphthalene		80 (4 hours) 115 (5 hours)	— —	— —	0 100

TABLE 4 (continued)

No.	System	Structural formula of product		Temperature (° C)	$k \cdot 10^4$	E (kcal/mole)	Extent of exchange (%)
1	2	3		4	5	6	7
17	Dimethylthiocarbamoyl tetrasulfide + S*	$(CH_3)_2N-\overset{S^*}{\overset{\|}{C}}-S^*-S^*-S^*-S^*-\overset{S^*}{\overset{\|}{C}}-N(CH_3)_2$	3	80 (6 hours)	—	—	0
				90 (6 hours)	—	—	~40
				110 (10 hours)	—	—	100
18	Zinc diethyldithiocarbamate + S* in decahydronaphthalene	$\left[(C_2H_5)_2N-C<^{S^*}_{S^*}\right]_2Zn$	4	120 (8 hours)	—	—	0
				150 (14 hours)	—	—	100
19	Lead diethyldithiocarbamate + S* in decahydronaphthalene	$\left[(C_2H_5)_2N-C<^{S^*}_{S^*}\right]_2Pb$	4	120 (5 hours)	—	—	30
				120 (32 hours)	—	—	100
20	Bismuth diethyldithiocarbamate + S* in decahydronaphthalene	$\left[(C_2H_5)_2N-C<^{S^*}_{S^*}\right]_3Bi$	4	120 (32 hours)	—	—	80
21	Nickel diethyldithiocarbamate + S* in decahydronaphthalene	$\left[(C_2H_5)_2N-C<^{S^*}_{S^*}\right]_2Ni$	4	150 (8 hours)	—	—	0
				180 (12 hours)	—	—	90
22	Sodium diisobutyldithiocarbamate + S*	$\left[(CH_3)_2CHCH_2-N-C<^{S^*}_{S^-}\right]Na$		74[6]	2.2		
				70[7]	2.2		
				60[8]	2.1		

TABLE 4 (continued)

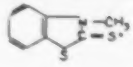
No.	System	Structural formula of product	Temperature (° C)	$k \cdot 10^4$	E (kcal/mole)	Extent of exchange (%)
1	2	3	4	5	6	7
23	3-Methyl-2-benzothiazolinethione + S^* in xylene (0.24 N)		158.4 170.3 180.4	0.18 1.1 1.96	42	
24	Ethyl dimethyldithiocarbamate + S^* (1:1) in decahydronaphthalene (0.31 N)	$(CH_3)_2N—\overset{\displaystyle S^*}{\overset{\|}{C}}—SC_2H_5$	147 153 160 172.5	0.3 0.6 1.8 6.1	42	
25	Ethyl diethyldithiocarbamate + S^* (1:1) in decahydronaphthalene (0.31 N)	$(C_2H_5)_2N—\overset{\displaystyle S^*}{\overset{\|}{C}}—SC_2H_5$	140 146 160 170 180	0.2 0.37 1.1 2.6 4.5	30.4	
26	Ethyl diisobutyldithiocarbamate + S^* (1:1) in decahydronaphthalene (0.31 N)	$(C_4H_9)_2N—\overset{\displaystyle S^*}{\overset{\|}{C}}—SC_2H_5$	139 149 160 170	0.9 2.0 4.0 9.0	25.6	
27	Ethyl isothiocyanate + S^*	$C_2H_5—N=C=S^*$ [5]	150 (5 hours) 178 (5 hours)	— —	— —	0 100
28	Phenyl isothiocyanate + S^*	$C_6H_5—N=C=S^*$ [5]	150 (5 hours) 178 (5.5 hours)	— —	— —	0 100

TABLE 5

DEPENDENCE OF THE RATE OF EXCHANGE WITH ELEMENTARY SULFUR ON CONCENTRATION

2-Mercaptobenzothiazole (C_m) + sulfur (C_s) in naphthalene, 131°			2-Benzothiazolyl disulfide (C_a) + sulfur (C_s) in naphthalene, 159°			Diisobutylthiocarbamoyl disulfide (C_i) + sulfur (C_s), in benzene, 136°		
C_s	C_m	$k \cdot 10^4$	C_s	C_a	$k \cdot 10^4$	C_s	C_i	$k \cdot 10^4$
0.12	0.24	0.58	0.09	0.18	1.2	0.2	0.1	2.8
0.24	0.24	0.58	0.18	0.18	1.3	0.4	0.1	3.0
0.72	0.24	0.56	0.36	0.18	1.2	0.8	0.1	2.8
0.24	0.12	0.33	0.90	0.18	1.1	0.4	0.025	1.8
0.24	0.24	0.58	0.18	0.09	0.9	0.4	0.1	2.8
0.24	0.72	1.2	0.18	0.18	1.3	—	—	—
—	—	—	0.18	0.36	2.1	0.4	0.2	3.8

of the exchange on the concentrations of reactants. The results obtained for three of these systems are given in Table 5.

The rate at which exchange occurs in these systems is almost independent of the concentration of sulfur, but it varies with the concentration of the organic compound. The concentration-dependence of the rate of exchange is more readily seen when the results are expressed graphically (Figure 2).

In the system, 2-mercaptobenzothiazole + sulfur, the rate of the exchange is independent of the sulfur concentration and directly proportional to the concentration of 2-mercaptobenzothiazole. In the systems, 2-benzothiazolyl disulfide + sulfur and diisobutylthiocarbamoyl disulfide + sulfur, the rate of the exchange is again independent of the sulfur concentration, but is proportional to the square root of the concentration of the second component. A depend-

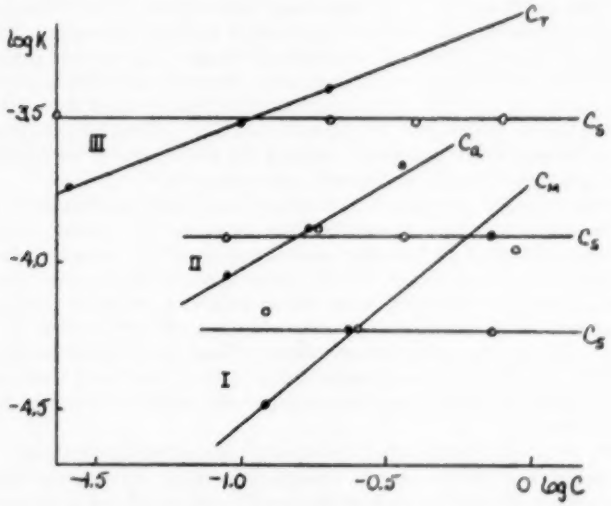


FIG. 2.—Dependence of the rate of the exchange reaction on the concentrations of reactants. 1) 2-Mercaptobenzothiazole + sulfur; 2) 2-benzothiazolyl disulfide + sulfur; 3) diisobutylthiocarbamoyl disulfide + sulfur.

ence of rate on concentration of this kind again allows us to postulate a radical mechanism for sulfur exchange in C—S bonds.

The tendency of sulfur in C—S bonds to undergo exchange is determined mainly by the strengths of these bonds, so that the activation energy for the exchange reaction is primarily determined by the C—S bond strength. The results for sulfur exchange in substituted 2-mercaptobenzothiazoles are interesting from this point of view (Systems 9, 10, 11, and 12 in Table 4). Substituents have almost no effect on the homolytic rupture of C—S bonds in these compounds. The character of the concentration dependence of sulfur exchange in 2-mercaptobenzothiazole (system 8) and in bis(2-benzothiazolyl) disulfide (system 5) and the similar activation energies of these systems indicate that the mechanism of sulfur exchange is the same in both compounds.

Comparison of the activation energies for sulfur exchange in bis(trichlorophenyl) disulfide (System 4) on the one hand and for sulfur exchange in various compounds having vulcanization-acceleration properties (Systems 5, 9, 13 and 14) on the other shows that there is a great difference in the C—S bond energies between these groups of compounds. It is possibe that this criterion—the ability to form radicals by fission at a C—S bond—is one of the most essential characteristics of vulcanizing agents and vulcanization accelerators.

Comparison of the results on sulfur exchange in various diethyldithiocarbamate salts (Systems 18, 19, 20, 21, and 22) gives an indication of the effect of the nature of the metal on the tendency of the sulfur in these compounds to undergo exchange. The variation observed is probably associated with the tendencies of the metals to form internal-complex compounds.

Sodium diisobutyldithiocarbamate occupies a special place among these salts (System 22). The readiness with which sulfur undergoes exchange with this compound depends on the identity of the solvent used.

In esters of dialkyldithiocarbamic acids (Systems 24, 25, and 26), unlike the salts of these acids and the corresponding thiocarbamoyl disulfides, only one sulfur atom—probably the C=S sulfur—takes part in exchange. The sulfur atom attached to ethyl does not undergo exchange. As regards the exchange of the sulfur of C=S bonds, i.e., thione sulfur, then, as can be seen from Table 4 (Systems 23, 24, 27, and 28), it occurs much less readily than that of the C—S sulfur of analogous compounds (Systems 9 and 13). Moreover, the mechanism of sulfur exchange in compounds containing the C=S bond is essentially different from that operating in compounds containing the C—S bond.

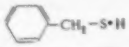
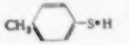
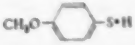
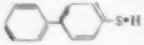
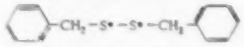
The rates of sulfur exchange in 3-methyl-2-benzothiazolinethione (System 23) and in ethyl dimethyldithiocarbamate (System 26) depend both on the concentration of sulfur and on the concentration of the organic component. Thus, when the concentrations of both components in the system, 3-methyl-2-benzothiazolinethione + sulfur, were varied to give a range of concentrations varying as 1:2:3:4, the exchange rate constant ($k \cdot 10^4$) varied as follows: 1.1:1.8:3.4:5.6, i.e., the kinetics were close to those for a bimolecular reaction. It is possible that in these compounds, which contain the C=S bond, exchange proceeds through the formation of a complex with sulfur, as has been suggested in the literature[6].

A more detailed discussion of the mechanism of sulfur exchange and the effect of molecular structure on the tendency for sulfur to undergo exchange in particular groups of compounds that we have investigated will be given in other communications.

In the course of the present work we have synthesized a large group of com-

TABLE 6

COMPOUNDS LABELED WITH RADIOACTIVE SULFUR

S^{35}-Labeled compound	Structural formula	Method of introducing S^{35}	Yield (%)
1	2	3	4
1-Butanethiol*	$C_4H_9S^*H$	$C_4H_9Br + NaS^*H$	80
α-Toluenethiol*		$C_6H_5CH_2Cl + NaS^*H$	75
p-Toluenethiol		*p*-Tolylmagnesium bromide + S_8*	20–25
p-Anisolethiol		Diazo compounds from *p*-anisidine + + $C_3H_5O—CS^*—S^*K$	70
4-Biphenylthiol		Diazo compound from 4-biphenylamine + $C_3H_6O—CS^*—S^*K$	70
Potassium ethylxanthate	$C_2H_5—O—CS^*—S^*K$	$Na_2S^* + CS_2 \rightarrow Na_2CS_3^* \rightarrow Na_2S^* +$ + CS_2^*; $CS_2^* + C_2H_5OK$	60–80
Ethyl disulfide	$C_2H_5S^*—S^*C_2H_5$	$2C_2H_5I + Na_2S_2^*$	80
Butyl disulfide	$C_4H_9S^*—S^*C_4H_9$	$2C_4H_9Br + Na_2S_2^*$	90
Benzyl disulfide		$2C_6H_5CH_2C + Na_2S_2^*$	90
p-Nitrophenyl disulfide		$2NO_2C_6H_4Cl + Na_2S_2^*$	70

* The synthesis of these compounds is described in the literature[4].

TABLE 6 (continued)

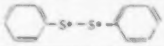
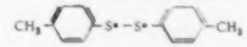
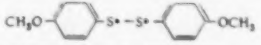
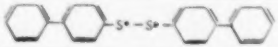
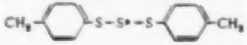
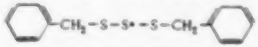
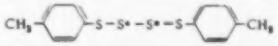
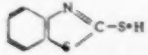
S^{35}-Labeled compound	Structural formula	Method of introducing S^{35}	Yield (%)
1	2	3	4
Phenyl disulfide		Phenylmagnesium bromide + $S_2{}^*Cl_2$	30
p-Tolyl disulfide		Oxidation of labeled *p*-toluenethiol	90
p-Methoxyphenyl disulfide		Oxidation of labeled *p*-anisolethiol	80
4-Biphenylyl disulfide		Oxidation of labeled 4-biphenylthiol	80
Ethyl trisulfide	$C_2H_5—S^*—S^*—S^*—C_2H_5$	$2C_2H_5I + Na_2S_3{}^*$	50
Ethyl trisulfide	$C_2H_5—S—S^*—S—C_2H_5$	Ethyl disulfide + $S_8{}^*$ (in $C_4H_9NH_2$)	40
p-Tolyl trisulfide		*p*-Toluenethiol + S^*Cl_2	80
Benzyl trisulfide		α-Toluenethiol + S^*Cl_2	80
p-Tolyl tetrasulfide		*p*-Toluenethiol + $S_2{}^*Cl_2$	60
2-Mercaptobenzothiazole		Exchange with $S_8{}^*$	80

TABLE 6 (continued)

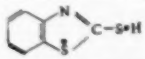
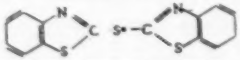
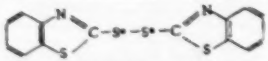
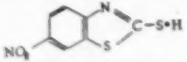
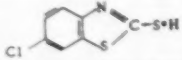
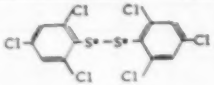
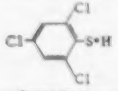
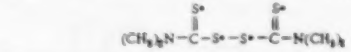
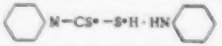
S^{35}-Labeled compound	Structural formula	Method of introducing S^{35}	Yield (%)
1	2	3	4
2-Mercaptobenzothiazole		Phenyl isothiocyanate + S_8^*	40
2-Benzothiazolyl sulfide		2-Chlorobenzothiazole + Na_2S^*	50
2-Benzothiazolyl disulfide		Oxidation of 2-mercaptobenzothiazole labeled in the thiol group	60
2-Benzothiazolyl disulfide		Oxidation of 2-mercaptobenzothiazole labeled in both sulfur atoms	60
2-Mercapto-6-nitrobenzothiazole		Exchange with S^*_8	70
6-Chloro-2-mercaptobenzothiazole		Exchange with S_8^*	70
2,4,6-Trichlorophenyl disulfide		Exchange with S_8^* with subsequent reduction to the thiol and reoxidation	50

TABLE 6 (continued)

S^{35}-Labeled compound	Structural formula	Method of introducing S^{35}	Yield (%)
1	2	3	4
2,4,6-Trichlorobenzenethiol		Reduction of mixture obtained in the exchange reaction between the disulfide and S_8^*	60
Dimethylthiocarbamoyl disulfide		Exchange with S_8^*	70
Piperidine pentamethylenedithiocarbamate		Piperidine and CS_2^*	80
Sodium diethyldithiocarbamate	$(C_2H_5)_2N—CS^*—S^*Na$	Exchange with S_8^*, or $(C_2H_5)_2NH + CS_2^*$	60
Sodium diisobutyldithiocarbamate	$(C_4H_9)_2N—CS^*—S^*Na$	Exchange with S_8^*	70
Thiourea	$(NH_2)_2C=S^*$	Exchange with S_8^*	50–30
Ethyl dimethyldithiocarbamate	$(CH_3)_2—N—C(=S^*)—CS_2H_5$	Exchange with S_8^*	80

pounds labeled with radioactive sulfur. A list of these compounds is given in Table 6, with indications of the method used for the introduction of the radioactive isotope into the molecule and the approximate yield of product. A more detailed description of some of these syntheses has been published previously[6]. Other methods for the synthesis of some of these compounds are described in the literature[7].

SUMMARY

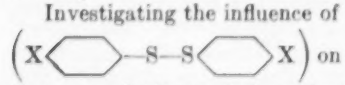
The method of labelled atoms offers very good opportunities for solving the problems of structure and reaction capacity.

The radioactive sulfur isotope S^{35} was used in the work to find out the influence the structure of molecules exerts on the mobility of sulfur atoms in the bonds S—S, C—S, C=S of organic polysulfides and a number of other compounds, including vulcanization accelerators.

We found that the intermediate sulfur atoms in organic polysulfides exchange comparatively easily with elementary radioactive sulfur, producing labelled polysulfides—R—S—S*—S—R. A number of compounds showed instances of a significant effect of the radical on the exchange capabilities of the intermediate sulfur atoms in organic trisulfides R—S—S*—S—R. The activation energy, for instance, of the exchange reaction of the intermediate sulfur atom in ditolyl trisulfide is equal to 14.5 Kcal/gmol and in diethyl trisulfide—27.3 Kcal/gmol.

The intermediate sulfur atoms in polysulfides likewise show capabilities of effecting an exchange with intermediate sulfur atoms of other polysulfides. This phenomenon, observed in model systems, occurs in certain vulcanized rubbers and has been investigated by a number of Soviet scientists.

Through a study of the mechanism of the reaction of the sulfur exchange between polysulfides, we established that these compounds exchange RS groups. A detailed examination of the temperature and concentration dependency of the rate of exchange of the RS groups between the RS̄—S̄R disulfides and the corresponding RSH thiols led to the conclusion as to the radical mechanism of these reactions and demonstrated that the reaction rate is chiefly determined by the stability of the S—S bond in the disulfides.

Investigating the influence of various substitutes (X) in diphenyl disulfide  on exchange capabilities of RS groups, we found that any substitutes, independent of their electrical charge, exert the same influence by sign on the behavior of the S—S bond of aromatic disulfides. In all cases, the S—S bond becomes stronger in comparison with the unsubstituted diphenyl disulfide. In order of influence the substituting groups can be arranged as follows: $H < CH_3 < OCH_3 < C_6H_5 < NO_2$. A conclusion was drawn that the regularity we observe is not a particular case peculiar to a homolytic break of the bonds of substituted aromatic compounds.

The exchangitivity of sulfur in compounds containing C—S bonds depends considerably on the structure of the molecules and is determined primarily by the durability of these bonds. Comparing the activation energies of sulfur exchange in hexachlordiphenyl disulfide (47.3 kcal/g-mole) with the activation energies of sulfur exchange in a number of compounds able to serve as vulcanization accelerators such as Altax (23 kcal g-mole), thiuram (21.5 kcal/g-mole), Captax (24 kcal/g-mole), we can see how different are the energies of the C—S bonds of these compounds. It is possible that this criterion, the ability to

form radicals by C—S bond, is one of the main criterions that characterize vulcanizing agents and accelerators of vulcanization.

The sulfur exchange in compounds containing C=S bonds, i.e., thion sulfur, is a far more difficult process than in similar compounds with the C—S bond and its mechanism is quite different.

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[3] Guryanova and Vasilyeva, *J. Phys. Chem.* **28**, 60 (1954); Guryanova, *J. Phys. Chem.* **28**, 67 (1954).
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THE KINETICS AND OCCURRENCE OF OPTIMUM VULCANIZATION *

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VULCANIZATION OF NATURAL RUBBER STOCKS WITH LOW SULFUR CONTENT

The fundamental reaction of vulcanization is the combination of a vulcanizing agent with rubber. The kinetics of this reaction is expressed by smooth curves. Simultaneously with the combining of the vulcanizing agent, in fact as a result of it, changes take place in a number of physical and chemical properties of rubber—solubility, modulus, tensile strength, and other indexes. Unlike the kinetics of combination of the vulcanizing agent, the changes in these properties are most often represented by curves having a maximum or minimum which characterizes the phenomenon of optimum vulcanization.

The extreme form which curves of changes of physical and chemical properties of rubber assume during vulcanization can be explained, in our opinion, by the fact that, during vulcanization, there is a competition between opposing reactions, of which one set are reactions of structure formation (i.e., increase of the molecular weight and the intensity of intermolecular reaction), and the others are destruction reactions. Thus, during vulcanization under factory conditions, at least two reactions take place: (1) the reaction between rubber and sulfur, and (2) the reaction between rubber and molecular oxygen introduced into the vulcanization mix by milling with the ingredients. The amount of oxygen present here in moles approaches the molar concentration of sulfur.

As a result of the reaction with sulfur, the tensile strength increases, not only because of the increase of intermolecular cohesive forces but also because of the formation of sulfur bridges between chains. Starting with the additive nature of intermolecular reactive forces and the fact that bridge sulfur is a linear function of the total amount of combined sulfur (Figure 1) in a sulfur reaction proceeding in isolation, we may write:

$$T^S = b_1 + a_1 \cdot S \qquad (1)$$

where T^S is the tensile strength; S is the amount of combined sulfur; and b_1 and a_1 are constants.

In natural rubber mixtures, the action of oxygen is destructive, since the strength of the vulcanizate drops in proportion to the quantity of combined oxygen:

$$T_0 = b_2 - a_2 \cdot O \qquad (2)$$

Under actual vulcanization conditions, both reactions proceed jointly, and the summation of their effects on tensile strength is expressed by combining

* Translated for Rubber Chemistry and Technology from *Issledovaniya v Oblasti Vysokomolekulyarnykh Soedinenii, Doklady k 6-oi Konf. po Vysokomolekul. Soedineniyam*, 1949, pages 102–116. This report presents a brief résumé of work which the author carried out together with B. K. Karmin, A. V. Dobromyslova, M. S. Fel'dshtein, N. Novikova, D. I. Pevzner, B. V. Lukin, and I. I. Goldberg.

Equations (1) and (2). A statistical look at the change of molecular weight under simultaneous structure formation and destruction processes leads to an equation of summation in the following form:

$$T = (b_1 + a_1 \cdot S)(b_2 - a_2 \cdot O) \quad \ldots\ldots (3)$$

According to the data of Lewis[1], the kinetics of sulfur combination is described by the equation:

$$S = S_0(1 - e^{-k_1\tau}) \quad \ldots\ldots (4)$$

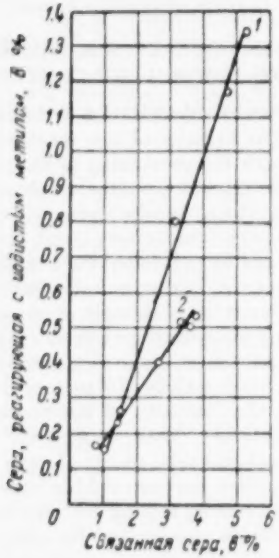

FIG. 1.—The relation between bridge and total combined sulfur in the vulcanizate. 1—Without accelerator. 2—Stock with diphenylguanidine. The abscissa represents the per cent combined sulfur; the ordinate the per cent of sulfur, determined by methyl iodide.

The kinetics of oxygen combination under conditions of high catalyst content may be described by an analogous equation:

$$O = O_0(1 - e^{-k_2\tau}) \quad \ldots\ldots (5)$$

Substituting (4) and (5) in Equation (3) and simplifying as necessary, we arrive at the equation for change in tensile strength:

$$T = T_0[1 + a \cdot S_0(1 - e^{-k_1\tau})][1 - b \cdot O_0(1 - e^{-k_2\tau})] \quad \ldots\ldots (6)$$

where T_0 is the strength of the raw stock; S_0 is the total sulfur content; O_0 is the oxygen content; k_1 is the kinetic constant for sulfur combination; k_2 is the kinetic constant for oxygen combination; and a and b are structural-strength constants which relate the change of tensile strength to the quantities of combined sulfur and oxygen, respectively.

The applicability of Equation (6) is confirmed in a number of examples of natural-rubber stocks, in cases where the total sulfur content was not more than 3 per cent. In Figure 2 are plotted the theoretical curves and the correspond-

ing experimental points. Figure 3 presents the experimental curve (*3*) of change of tensile strength during vulcanization of a mixture containing mercaptobenzothiazole. In accordance with Equations (1), (2), (4) and (5), and with constants calculated from the kinetic curve of tensile strength, the probable kinetic curves of combination for sulfur and oxygen were constructed, as well as curves of the change of tensile strength resulting from sulfur (T^S) and oxygen (T^O) combination. The accuracy of this representation of the kinetics of component reactions is confirmed by: (1) the coincidence of experimental

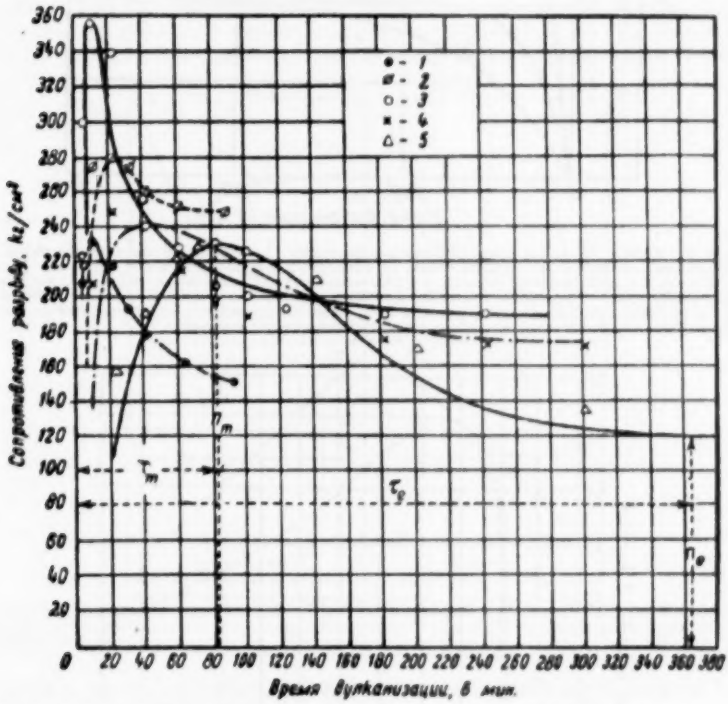

FIG. 2.—The change of tensile strength of stocks with various accelerators during vulcanization. 1—Dimethyldithiocarbamate; 2—Heptaldehyde-aniline; 3—Tetramethylthiuram disulfide; 4—Mercaptobenzothiazole; 5—Diphenylguanidine. The abscissa represents time of vulcanization in minutes; the ordinate the tensile strength in kg. per sq. cm.

points for the combination of sulfur with the theoretical curve and (2) agreement of the activation energy for the presumed oxidation reaction in vulcanization (11,000 cal./mole) with the experimentally determined activation energy for the oxidation reaction in rubber under the same conditions (12,000 cal./mole). Direct proof of the explanation of the phenomenon of optimum vulcanization proposed by us was afforded by experiments under conditions where molecular oxygen was completely excluded from the stock being vulcanized. In Figure 4, curve *1* presents the change of tensile strength of a stock containing 1.9 per cent sulfur with mercaptobenzothiazole as the accelerator for the case of its vulcanization in the form of thin strips (the reaction vessel being evacuated at

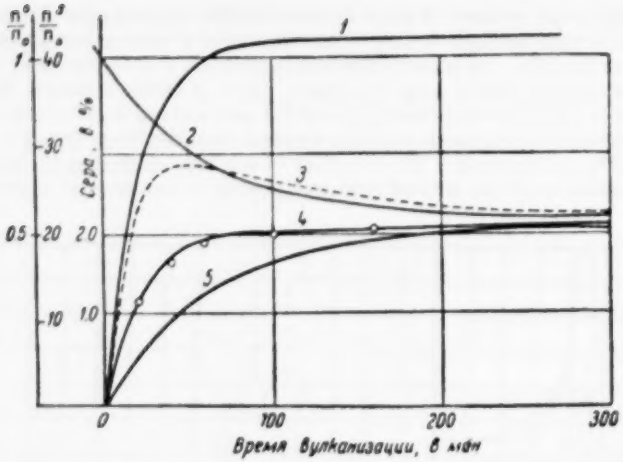

FIG. 3.—Kinetic curves for mercaptobenzothiazole stocks. 1—Theoretical curve of the change of tensile strength resulting from combined sulfur; 2—That resulting from reaction with oxygen; 3—Experimental curve of change in tensile strength; 4—Theoretical curve of combination with sulfur; 5—That of oxygen combination. The abscissa represents time of vulcanization in minutes; the two left scales of the ordinate represent ratios of strengths resulting from combined oxygen and sulfur, respectively, to the strength of the raw stock, while the scale on the right represents per cent sulfur.

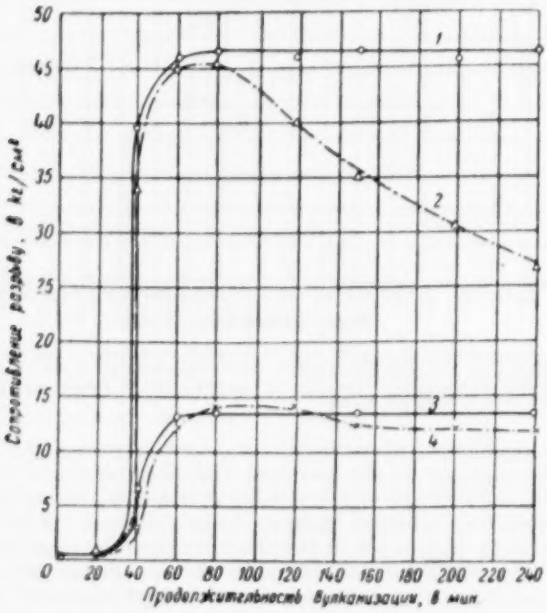

FIG. 4.—Change of the tensile strength of natural rubber during vulcanization. 1—In an atmosphere of nitrogen; 2—In air and in the vulcanization of sodium-butadiene rubber; 3—In nitrogen; 4—In air. The abscissa represents the length of vulcanization time in minutes; the ordinate the tensile strength in kg. per sq. cm.

room temperature for a period of 10 hours with a mercury pump and then filled with pure nitrogen); curve *2* shows this for the case of vulcanization of these same strips in a reaction vessel full of air. It can be seen that the exclusion of oxygen from the vulcanized stock causes the maximum in the kinetic curve of tensile strength to be eliminated; in other words, the phenomenon of optimum vulcanization disappears. Curves *3* and *4* describe analogous experiments on sodium-butadiene rubber stocks. In this case no difference between curves was observed, for a reason which is fully understood and explained below.

Figure 5 shows the influence which the individual reactions of structure formation and destruction exert on the parameter of the kinetic curve of change of tensile strength and, in particular, on the maximum strength (T_m) and on the time for optimum vulcanization (τ_m). It is seen that an increase of the constant

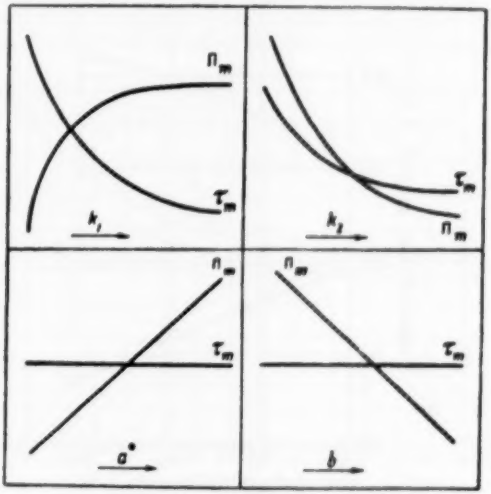

FIG. 5.—Diagram of change of tensile strength at optimum vulcanization (T_m) and the time required to reach optimum vulcanization (τ_m), as dependent on the change of the constants k_1, k_2, a, and b of the basic Equation (6).

of speed k_1 for the combination of sulfur, when the rest of the factors are kept constant, brings about a rise of the maximum tensile strength (T_m) and a drop in the time required to reach optimum vulcanization (τ_m). An increase of the kinetic constant of the oxygen reaction (k_2) causes a drop in tensile strength at optimum vulcanization and also shortens the time for optimum vulcanization. A change of the constants a and b does not affect the time required for optimum vulcanization, but rather seems to affect the maximum tensile strength appreciably.

This effect of the individual reactions on the general character of the kinetics of change of tensile strength during vulcanization can be detected through the action of accelerators, which changes not only the constant (k_1) of the speed of the sulfur reaction, but also the constant (k_2) of the speed of the reaction with oxygen. We had established[2] that mercaptobenzothiazole accelerates, but that thiuram and diphenylguanidine retard, the oxidation reaction in rubber. Investigation of changes of viscosity and molecular weight (by osmosis) shows

that mercaptobenzothiazole not only accelerates the reaction of union with oxygen, but also promotes the scission of molecular chains in natural rubber; the combined oxygen content being the same, the viscosity of a solution of rubber containing mercaptobenzothiazole drops more sharply than that of one where the oxidation takes place in its absence. Hence, mercaptobenzothiazole should be considered to be an agent which greatly increases the value of the kinetic constant, k_2, of the oxygen component of the vulcanization process. Thiuram, on the contrary, decreases the value of the constant k_2, while increasing the kinetics of the sulfur reaction. The result of this, as is seen in Figure 5, is that stocks with thiuram show an increased tensile strength at optimum vulcanization in comparison with mercaptobenzothiazole stocks (Figure 2).

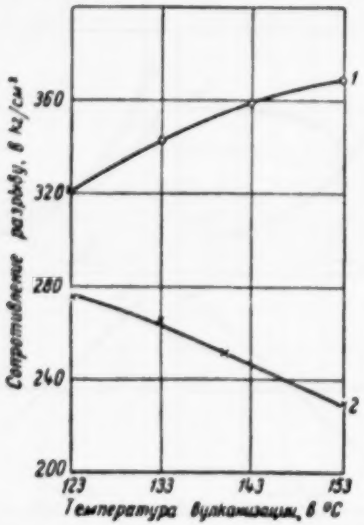

FIG. 6.—Effect of vulcanization temperature on tensile strength at optimum vulcanization in stocks with different accelerators. 1—Thiuram; 2—Mercaptobenzothiazole. The abscissa represents vulcanization temperatures in ° C, the ordinate tensile strength in kg. per sq. cm.

The effect of vulcanization temperatures on the tensile strength at optimum vulcanization in stocks containing different accelerators in equimolar amounts, is especially characteristic. From Figure 6 it is evident that stocks differing only in their accelerator have temperature coefficients of vulcanization which differ in sign. Such an effect could not occur if the change of tensile strength during vulcanization proceeded under the operation of only one factor. But with the interaction of two reactions at cross-purposes—structure formation and destruction—each of which has a separate positive temperature coefficient, the overall process may possess both positive and negative temperature coefficients, depending on the corresponding temperature coefficients and speeds of the individual reactions. For example, in a thiuram stock a rise in temperature leads to an increase of tensile strength at optimum vulcanization, because this accelerator increases the speed of the combining reaction with sulfur and slows down the reaction with oxygen. In stocks containing mercaptobenzothiazole, a rise of temperature lowers the tensile strength of the vulcanizate as a con-

sequence of intensifying the destruction reaction in relation to the reaction of structure formation.

As for the characteristics of the accelerators, we must point out that their influence is felt likewise on the structural-strength coefficients a and b of the basic Equation (6). This influence is connected with the fact that the accelerators give rise to some sort of sulfur compounds in the vulcanizate. Little is known as yet of the types of these compounds. However, by using the method of Selker and Kemp[3], we were able to establish that the introduction of mercaptobenzothiazole in the vulcanization of sodium-butadiene rubber increases the bridge sulfur content from 2 to 6 per cent of the total sulfur content. In natural rubber stocks this effect of accelerators is less marked, apparently because the commercial product already contains natural accelerators.

From the presentation which we have put forward regarding the mechanism of vulcanization, it may be presumed that antioxidants introduced into a stock exert an influence not only on the aging (oxidation) of finished rubber products

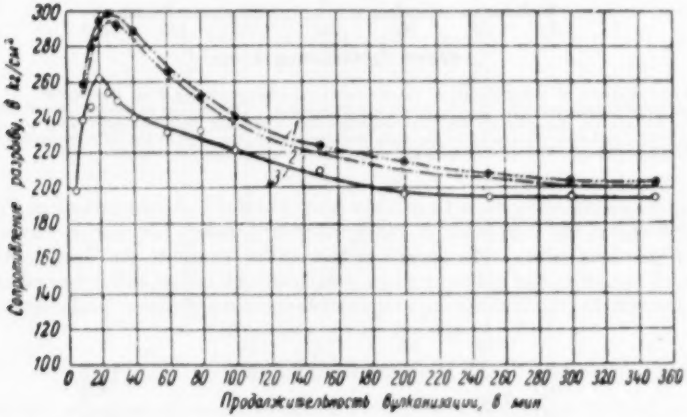

FIG. 7.—Effect of an antioxidant (Tonox) on the kinetics of change of tensile strength. 1—Stock with 0.5 part by wt. of Tonox; 2—Stock with 1 part Tonox; 3—Stock without Tonox. The abscissa represents time of vulcanization in minutes; the ordinate the tensile strength in kg. per sq. cm.

in service, but also on the parameters of the kinetic curves of vulcanization. Actually, as can be seen in Figure 7, the addition of Tonox (p-p'-diaminodiphenylmethane) raises the tensile strength value at optimum vulcanization (T_m) and lengthens the time for optimum vulcanization (τ_m). This action by Tonox is related to the fact that it is an oxidation inhibiter, and that, in its presence, the kinetic constant for the reaction of oxygen combination, k_2, in Equation (6) decreases to a value of 0.020, instead of 0.034 for the case of vulcanization of the same stock without Tonox. According to the system depicted in Figure 5, this should also bring about an increase of T_m and τ_m.

VULCANIZATION OF STOCKS WITH HIGH CONTENT OF STRUCTURIZING AGENT

The kinetic Equation (6) which we propose describes and explains fairly accurately the nature of vulcanization of natural rubber with a low sulfur content (3–5 per cent). However, as experiments show, it does not hold good

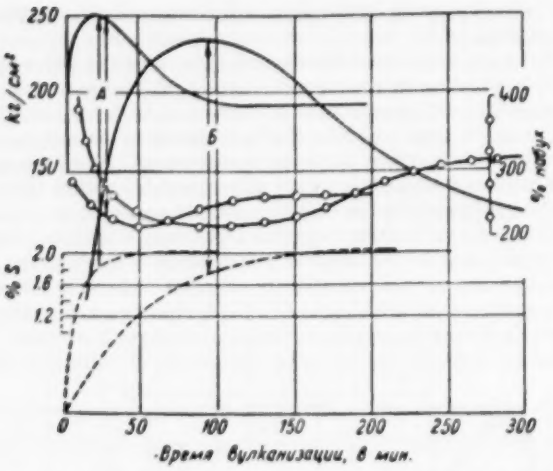

FIG. 8.—Kinetics of vulcanization of natural rubber stocks containing 2 per cent sulfur. A—Stock with mercaptobenzothiazole; B—Stock with diphenylguanidine. The abscissa represents time of vulcanization in minutes. On the ordinate, the upper left-hand scale represents tensile strength in kg. per sq. cm.; the lower left-hand scale represents the per cent combined sulfur; the scale at the right represents the per cent swelling. These correspond to the solid, dotted, and beaded lines, respectively.

with stocks containing more than 5 per cent of sulfur. A comparison of Figures 8 and 9 shows the difference in vulcanization: kinetics between stocks with 2 and 7 per cent sulfur. In stocks of low sulfur content, the drop in tensile strength comes at the moment when practically all of the sulfur has combined with the rubber; the descending loop corresponds to a period of prolonged action

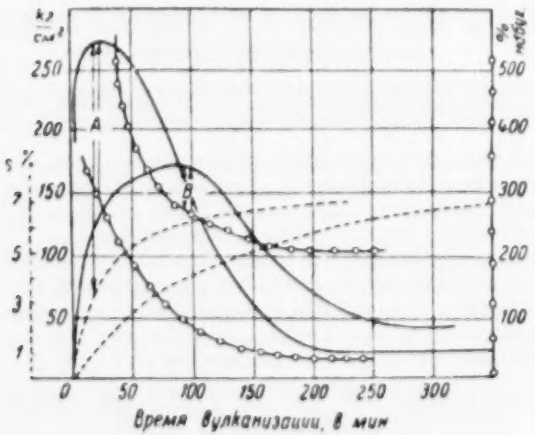

FIG. 9.—Kinetics of vulcanization of natural rubber stocks containing 7 per cent sulfur. A—Stock with mercaptobenzothiazole; B—Stock with diphenylguanidine. The abscissa represents time of vulcanization in minutes. In the ordinate, the upper left-hand scale represents tensile strength in kg. per sq. cm.; the lower left-hand scale represents the per cent sulfur; the scale at the right represents the per cent swelling. These correspond to the solid, dotted, and beaded lines, respectively.

of oxygen as a destructive agent. For this reason, the kinetic curve representing the swelling ability of a vulcanized stock in gasoline has a minimum which coincides in time with the maximum of tensile strength. However, when stocks with high sulfur content are vulcanized, the maximum tensile strength is reached at a point before the sulfur is wholly consumed—namely, when the combined sulfur amounts to 3.5 per cent on the rubber. The swelling curve for this case is a smooth one, descending to the limiting value. This sort of change in properties of a stock indicates that, as a result of prolonging the sulfur combination beyond the optimum vulcanization point, the reactions of structure formation become dominant over the destructive action of oxygen. In order to clarify the maximum on kinetic curves for these cases, we may adopt the following hypotheses[4].

It is known that the tensile strength of vulcanizates depends on the amount of the crystallized phase present; that is, in general, on the amount of the highly oriented portion of the rubber which is created under tension at the moment of

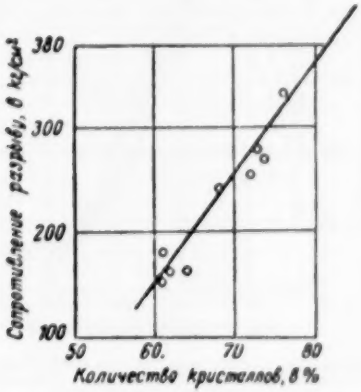

FIG. 10.—Dependence of the tensile strength of a vulcanizate on the amount of the crystalline portion which is created by an elongation of 500 per cent (for vulcanizates of various compositions). The abscissa represents the percentage of crystals; the ordinate the tensile strength in kg. per sq. cm.

breaking. This is evident from Figure 10, where the tensile strength of vulcanizates which differ from one another in type of accelerator and sulfur content approximate, at optimum vulcanization, a linear function of the crystallized phase[5]. Crystallizing ability, in turn, depends on the inner structure of the vulcanizate. In a raw plasticized stock no crystallization takes place under tension, because of the occurrence of plastic flow. The creation of a crystallized phase becomes possible after the vulcanizing agent, establishing local bonds between chains, eliminates plastic deformations. The density of the vulcanizate network rises as the content of structure forming agent increases, besides which the strength of the network grows. However, the tensile strength of the network rises only as long as its density does not become so appreciable as to hamper the movements and orientation of the molecular chains, thus reducing the quantity of the crystallized or highly oriented phase present. In the case of natural rubber vulcanizates, this position is reached when about 3.5 per cent of sulfur is combined with the rubber. When this point of optimum vulcanization has been reached, a decline of tensile strength is observed.

An interpretation of this sort is confirmed by the following interesting fact, observed only in stocks high in sulfur. If the tensile strengths of vulcanized stocks are determined at different speeds, we note not only a change in the absolute indexes but also a displacement of the optimum point in vulcanization time (Figure 11). This displacement is explained by the fact that as a result of relaxation, particularly in the molecular chains, a higher speed of deformation means a larger number of chains in the oriented condition. Hence, the more rapid the deformation, the lower the network density at which a maximum can be reached on the tensile strength curve.

The concept of an influence exerted by the density of a vulcanization network on the tensile strength of the vulcanizate does not contradict the previous discussion regarding the presence in vulcanization of varidirectional reactions of structure formation and destruction. Further, the increase of network density

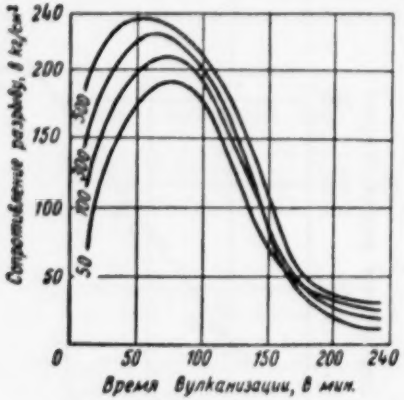

FIG. 11.—Change of tensile strength of stocks with 7 per cent sulfur during vulcanization. The figures on the curves indicate the deformation speed in mm. per minute. The abscissa represents vulcanization time in minutes; the ordinate the tensile strength in kg. per sq. cm.

can give rise to a maximum on the tensile strength curve, but cannot explain the occurrence of special points on the curves of swelling, solubility, and modulus.

The class of stocks into which rubber stocks high in structure forming agent fall also includes ordinary (2 per cent sulfur) stocks of sodium-butadiene rubber and of other kinds of butadiene polymers containing double bonds which are principally in vinyl side-groups, with the 1,2-structure. As we have shown[6], these rubbers become insoluble, elastic, and strong even in the early stages of oxidation. Such a change in properties is connected with the creation, in the chains, of a large number of oxygen-containing functional groups, which increase the intermolecular attraction between chains and within chains, and also insure the formation of hydrogen bonds or bonds which are chemically of the ether type, between chains. The latter is demonstrated by the appearance of narrow absorption bands at wave lengths[7] of about 8.5μ and likewise by the rise of the (osmometric) molecular weight during oxidation. Thus it is that oxygen, in the case of sodium-butadiene rubber, plays a role similar to that of sulfur as a structure forming agent. This is why, in sodium-butadiene rubber stocks, the maximum either does not appear at all or else is observed only in kinetic curves

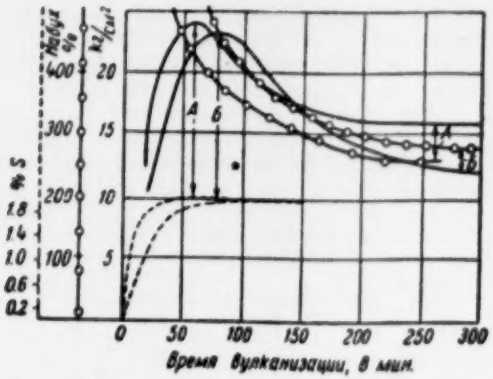

FIG. 12.—Kinetics of vulcanization of sodium-butadiene stocks containing 2 per cent sulfur. A—Stocks with mercaptobenzothiazole; B—Stocks with diphenylguanidine. The abscissa represents vulcanization time in minutes. In the ordinate the left-hand scale represents per cent combined sulfur, the middle scale per cent swelling, and the scale on the right tensile strength in kg. per sq. cm. These correspond to the dotted, beaded, and solid lines, respectively.

of change of tensile strength. The rest of the properties (swelling, modulus) show their change in smooth curves (Figures 4 and 12).

An intermediate position, with respect to the character of vulcanization kinetics, between natural rubber and sodium-butadiene stocks is occupied by butadiene-styrene rubbers of the Buna-S type. In these rubbers, apparently, the double bonds are located chiefly in the main chains, with a 1,4-structure. Thus, in these rubbers the oxygen at a certain stage can play a role of destructive agent like that in natural rubber. We traced structural changes under vulcanization in natural and butadiene-styrene rubbers through the change in the modulus of two-dimensional stress, which, according to Treloar[8], has the following form:

$$\sigma = N \cdot k \cdot T \qquad (7)$$

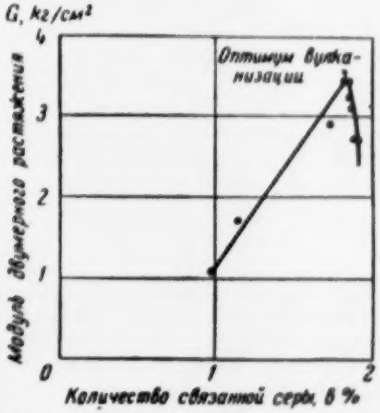

FIG. 13.—Change of the two-dimensional stress modulus as a function of the sulfur content, in natural rubber vulcanization. The abscissa represents the per cent combined sulfur; the ordinate the two-dimensional stress modulus in kg. per sq. cm. The peak of the curve represents optimum vulcanization.

where N is the number of sections (molecular chains) between junctions of the vulcanization network and k is the Boltzmann constant.

In natural rubber stocks, the two-dimensional stress modulus increases according to the increase in combined sulfur up to the moment of optimum vulcanization; after this point, in spite of the still-continuing combination with sulfur, the modulus sharply declines; this indicates the course of the oxidative destruction reaction (Figure 13). In butadiene-styrene rubber stocks, the modulus curve is more complex in form; after the optimum moment there is a slight drop, after which comes a sharp rise (Figure 14). This rise is, no doubt, connected with the structure forming action of thermal oxidation reactions.

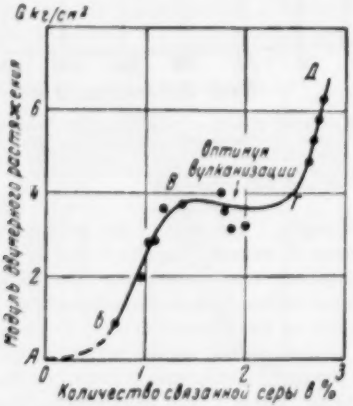

FIG. 14.—Change of the two-dimensional stress modulus as a function of the sulfur content of butadiene-styrene rubber vulcanizates. The abscissa represents the per cent combined sulfur; the ordinate the two-dimensional stress modulus in kg. per sq. cm. The arrow indicates optimum vulcanization.

Beginning with Equation (7), we may trace the quantitative change in vulcanizate network junctions. It is not hard to understand that the creation of each new junction in the existing network increases the number of sections between chains by a factor of 2. Thus:

$$\frac{dN}{dn} = 2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

where n is the number of junctions in the network. Assuming now that junctions consist of single atoms of sulfur and that the bridge monosulfide sulfur is a linear function of the combined sulfur (Figure 1), we may write:

$$S = \frac{S_M}{\gamma} = \frac{n \cdot m \cdot 100}{\gamma \cdot \rho} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

where S is the percentage of combined sulfur; S_M is bridge sulfur; γ is a coefficient relating combined sulfur to bridge sulfur; n is the number of monosulfide bridges in one cc. of the vulcanizate; m is the weight of an atom of sulfur; and ρ is the density of the vulcanizate. Making use of Equations (7), (8), and (9), we arrive at the expression:

$$\frac{d\sigma}{dS} = \gamma \cdot \frac{K \cdot T \cdot \rho}{50 \cdot m} = 14.1 \times 10^6 \gamma \text{ dynes/cm}^2/1\% \ S \quad \ldots\ldots\ldots\ldots (10)$$

Calculation of the coefficient γ for the rectilinear portion of the modulus curve for natural-rubber stocks gives a value of 0.19. This figure corresponds to an analogous amount which we determined to be the quantity of monosulfide bridge sulfur, by means of the Kemp method of reaction with methyl iodide (for the reaction with methyl iodide, $\gamma = 0.21$). In butadiene-styrene rubber stocks the monosulfide sulfur, determined by the methyl iodide method, amounts to about 22 per cent. This figure is considerably lower than the figure corresponding to the coefficient γ, determined through the two-dimensional stress modulus (for the final portion $\gamma = 0.76$).

It is evident that the two-dimensional stress modulus expresses all kinds of cross-connections, while the methyl iodide method determines only the monosulfide bonds. For this reason, in vulcanizates of those kinds of rubbers in which oxygen plays the part of a structure forming factor, the coefficient γ, determined through moduli, should be greater than the figure obtained by reaction with methyl iodide.

Thus we may conclude that the character of change in the two-dimensional stress modulus is in complete agreement with the concepts developed in regard to the kinetics of vulcanization and the mechanism of the phenomenon of optimum vulcanization.

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FAILURE OF STRETCHED RUBBERS UNDER THE INFLUENCE OF OZONE *

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Cracks perpendicular to the axis of stretching rapidly appear on stretched or bent rubbers exposed to the atmosphere (in the case of loaded vulcanized polybutadiene in the spring and summer months, in a few days). The fundamental cause of this phenomenon is the action of the ozone which is always present in the atmosphere in concentrations of several millionths of a per cent. However, we still lack any clear idea of the mechanism of this phenomenon, which would make possible a rational determination of ways to protect rubber. Questions related to the mechanism of ozone cracking of rubbers are discussed in this article on the basis of new experimental data.

Causes of the formation of cracks. The presence of a stress is an indispensable condition for ozone deterioration. It is believed that the role of the stress can be summed up as follows[1].

1. The rubber molecules, under the influence of stress, are activated with respect to ozone.

2. The stress modifies the relation between the processes of structure formation and destruction in favor of the latter. For example, the stress may facilitate rupture of the chains during regrouping of the initial unstable ozonide into isoozonide[2].

Both these assumptions are still unproved. It has been established experimentally that ozone also reacts with relaxed vulcanized rubber[3] and unvulcanized rubber[4]. However, because of the easy decomposition of ozone in contact with the surface of substances, the reaction is greatly retarded after the formation of a surface film of ozonide.

It is known that the reaction of ozone with rubber in solution is accompanied by rupture of the chain during regrouping of the ozonide into isoozonide. We may assume that in the reaction of hard rubber with ozone this process will also take place, but to a lesser degree; consequently, "molecular" cracks must form on the surface. This evidently occurs in such rubbers as natural and Butyl rubber, which are subject principally to destruction. A very pronounced structure formation, with the appearance of a brittle film on the surface, is observed in the reaction of purified polybutadiene in the relaxed state with ozone[4].

The deforming stress has a double role in the ozonization of rubbers.

1. The stress opens old cracks wider, and if the ozonide layer is not very elastic, it causes the latter to crack, too. As the cracks open at separate points on the surface film, any obstruction to diffusion is decreased and the reaction with ozone continues, leading to further development of cracks. This aspect of the action of the stress is characteristic of rubbers and consists in apparent activation and acceleration of the reaction between ozone and rubber. Appar-

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ent activation can take place not only during the action of stress. A similar phenomenon was observed in the ozonization of relaxed polybutadiene, butadiene-styrene and butadiene-acrylonitrile rubbers containing carbon black and immersed in acetic acid or chloroform, that is, under conditions where the entire surface film is continuously removed. In this case the rubber dissolves forming carbon black suspensions.

The explanation of ozone deterioration on the basis of theories of the activation of rubber by stress seems unfounded to the authors, since: (a) this does not explain the unique character of rubber deterioration (cracking); (b) according to published data[5] it is hardly possible to regard the activating role of stress in ordinary low-molecular rubbers at low deformations (1.5–2 per cent) as sufficient for ozone cracking; (c) the process would have to be activated in this case by any kind of stress, especially compression.

We have shown, however, that the surface of rubber subjected to pure compression is not susceptible to ozone cracking. The experiment was conducted in the following manner. A rubber plug (I) made of compounded polybutadiene

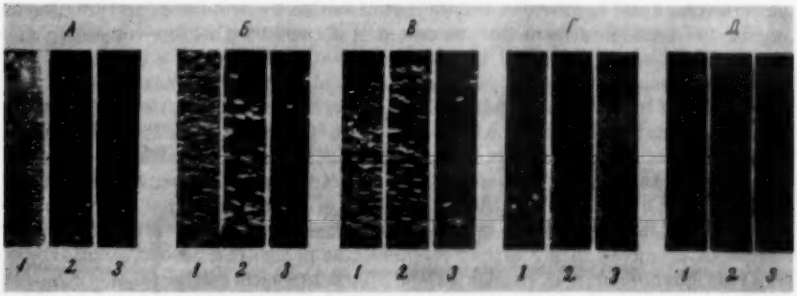

FIG. 1.—Double ozonization of vulcanized rubbers in relaxed, then in stretched state. A—SKN-26; B—SKB; C—SKS-30; D—Neoprene; E—Natural rubber. The specimens after ozonization for 40 minutes at 20% elongation; ozone concentration 0.0025% (for Neoprene the ozone concentration was 0.08% and the time 55 minutes). 1—Control sample. 2 and 3—Ozonized in relaxed state 6 hours; ozone concentration 0.3%. 3—Stretched to 100% every 2 hours.

rubber was forced into a metal tube so as to be flush with the end of the tube, with only the end of the plug exposed; the plug was under a radial compression of 15 per cent. Into the other end of the tube, for comparison, another rubber plug (II) was inserted so that it protruded partly from the tube and was under 15 per cent compression. Both plugs were subjected to the action of ozone at a concentration of 0.1 per cent. After 4 minutes, a deep circular crack appeared at the bend, i.e., at the rim of the tube, on plug II. On plug I, the end of which was under pure compression, there was no change at all, even after 90 minutes.

What proof is there of the formation of a brittle ozonide film on the surface of most synthetic elastomers? It is known that polybutadiene ozonide is a solid[6]; on the basis of existing data, butadiene-acrylonitrile rubber[7] and polychloroprene[8] ozonides are also solid. Furthermore, the following experiment confirms the hypothesis. Specimens of loaded polybutadiene rubber, SKN-26, butadiene-styrene copolymer, and Neoprene were ozonized without stretching in a current of ozonized air (ozone concentration 0.3 per cent) for 6 hours. One group of specimens was stretched 100 per cent after every 2 hours and then relaxed. After ozonization, the specimens were stretched 30 per cent and

placed in an ozone atmosphere of lower concentration (about 0.001 per cent) with a control sample. Since microcracks appear on rubber which has been ozonized without stretching, one would expect that, when the stress is removed, they would become loosely connected during the second deformation, owing to the brittleness of the surface film, and ozonization of the lower layer of rubber would take place. When such specimens, stretched 30 per cent are ozonized, no cracks, or very few, should appear. This was observed by the authors for the rubbers mentioned (see Figure 1).

This effect was not observed for natural rubber (Figure 1*e*) and Butyl rubber (that is, the nature of the deterioration was the same in all specimens). This agrees with the fact that natural rubber ozonide is a heavy oil[9], and Butyl rubber ozonide is also apparently a liquid, since the surface of Butyl rubber after ozonization becomes very sticky.

2. The second aspect of the action of a stress is common to all solids: the deforming stress causes the formation of cracks in rubber (surface cracks according to Bartenev[10]), leading to rupture. In the case of rubbers, this action of the stress is accelerated by the influence of ozone. The relationship between the cracking (and rupture) of brittle materials due to stretching, and the cracking of vulcanized rubbers due to ozone is shown by the following. In the action of ozone on stretched loaded vulcanizates of natural, SKS, SKB, and SKN rubbers, immersed in glacial acetic acid and carbon tetrachloride, no deterioration by ozone was observed, even after several hours, despite the comparatively high concentration of ozone, viz., 0.3 per cent. Under ordinary conditions, in air, the specimens crack in 10–15 minutes in the presence of ozone concentrations 500 times smaller. The tremendous increase in resistance of rubbers to ozone deterioration in this case is due to the fact that the surface film formed on vulcanizates under the influence of ozone, and having microcracks, is dissolved in the carbon tetrachloride or acetic acid.

This phenomenon is similar to the sharp increase of the tensile strength (400 times) of rock salt, observed by A. F. Joffe when the surface layer of a crystal containing microcracks is dissolved in water. A similar increase of tensile strength was observed by Zhurkov when glass fibers were corroded by hydrofluoric acid[11].

Conditions which favor ozone deterioration in rubbers. Evidently the fundamental conditions necessary for and favoring the formation of cracks on vulcanizates under the influence of ozone are:

1. The presence of reactive segments in the rubber phase of the vulcanizate (evidently the double bonds are such segments).
2. The presence of directed mechanical stresses (causing extension but not compression) in the rubber.
3. The unique character of the chemical reaction of vulcanized rubber with ozone, which is accompanied in particular by rupture of the hydrocarbon chain, formation of a low-elastic surface film (in this case, where the ozonides are solid), and is characterized by the absence of ozone diffusion inside the specimen.

Ozone deterioration is not only a chemical, but at the same time a physical process; hence the identity of the ozone resistance of vulcanizates with their resistance to ozone deterioration is incorrect. This identity of the properties has been made in scientific literature[12]. Two examples clearly demonstrate the difference between the chemical resistance of rubber to ozone and its resistance to ozone deterioration.

TABLE 1

CRACKING OF VULCANIZATES BY OZONE AT LOW TEMPERATURES

	Natural Hevea	Natural kok-saghyz	Gutta	SKB	SKS-30	SKN-26
Temperature (° C) at which cracks appear	−35°	−30°	−5°	−15°	−10°	+5°
Temperature at which cracks do not appear t_1	−40°	−40°	−10°	−20°	−15°	0°
Relative vitrification temperature t_2	−55°	−55°	−30°	−40°	−40°	−20°
$t_2 - t_1$	15°	15°	20°	20°	25°	20°

(a) The example cited earlier of the absence of cracking during ozonization in rubbers deformed in liquids, while cracking takes place in air, although in both cases the chemical properties of the rubber and the stress applied are the same.

(b) When the temperature is increased from 20° to 50°, the rate of appearance of the cracks increases only 1.4 times[12], while the rate of the chemical reaction should increase 8 times. When the temperature is reduced to −50° (experiments were not made at lower temperatures), a rapid chemical reaction was observed between ozone and various carbon-black rubbers in chloroform, judged by the formation of carbon-black suspensions. At the same time, cracking ceased in rubbers at higher temperatures, i.e., 15–20° above the conventional vitrification point (see Table 1). (The rubbers were tested by stretching to 20 per cent deformation; the ozone concentration was 0.4 per cent.) Observations were continued 1 hour after the appearance of cracks. The relative vitrification temperature was determined as the temperature at which the residual deformation of a rubber stretched 20 per cent was 100 per cent after 10 minutes at the given temperature.

The unique character of the chemical reaction with ozone is confirmed by the absence of cracks during the action of such active reagents as iodine, bromine, or nitrogen peroxide fumes, and concentrated sulfuric acid on stretched or swollen vulcanizates. A hard slightly elastic film appears on the surface.

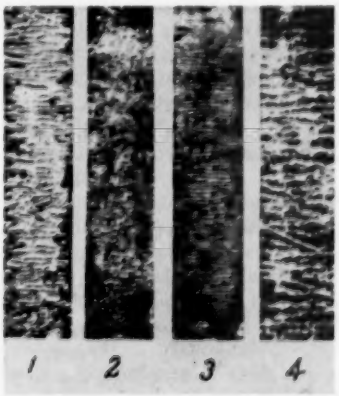

FIG. 2.—Vulcanized natural rubber (*1*), SKB rubber (*2*, *3*) and SKN-26 rubber (*4*) after having been treated, in the deformed state, with bromine (*1*, *2*), iodine (*3*), and nitrogen dioxide (*4*).

When the stress is removed from the specimens, the film is wrinkled and forms folds (see Figure 2). In distinction to ozone, these reagents penetrate very deep (we observed the formation of a surface layer more than 100μ thick), and the hardness of the entire specimen increases sharply, while ozone acts only on the cracks on the fresh surface of the rubber.

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THE MECHANISM OF OXIDATION OF SYNTHETIC RUBBERS *

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The complex chemical reactions underlying the thermal oxidation of rubbers develop in two opposite directions; oxidative destruction, which involves a scission of the main valence chains (oxidative destruction); and the formation of branched structures (polymerization). The final result of these reactions in rubbers is a profound irreversible change which appears outwardly as the loss of some commercially valuable properties (elasticity, solubility, etc.).

The aim of the present report is to explain some results of an investigation of the kinetics and intermediate products of the oxidation of a sodium-butadiene polymer[1].

Strips of polymer 30–40μ thick were subjected to oxidation. The method of purifying the polymer and preparing strips, as well as the apparatus and method of studying oxidation are described in detail in a paper which the authors devoted especially to this[2].

During the oxidation of the polymer in the temperature range of 80–100° C, solid, liquid, and gaseous reaction products are formed. The proportions of these products change with the degree of oxidation and the temperature. Figure 1 presents curves of the evolution of volatile matter[3] in the oxidation process. In shape these are reproductions of the kinetic curves of oxidation. The volatile products include formic acid and formaldehyde. They are produced chiefly by the oxidative decomposition of double bonds in the side chains. The loss of unsaturation in the side chains during oxidation, determined from ozonolysis data, is equal to the loss of unsaturation, calculated from the quantity of volatile matter formed[4].

Thus, for example, as a result of complete oxidation of the polymer at 90° C, the loss of unsaturation in the side chains equaled 11.2 per cent (ozonolysis data), while that calculated from the volatile products was 11.0 per cent.

Of the total consumption of oxygen in oxidation of the polymer (650 millimoles/mole), only 200 millimoles/mole[5] is converted into volatile products. The data presented show that oxidation extends only in a limited degree to the double bonds in the side chains.

We showed that the presence of volatile products in the reaction zone exerts virtually no influence on the course of the reaction.

In the temperature range indicated above, adequately reproducible results on oxidation kinetics were obtained. The sum of the weights of the oxygen and rubber entering into the reaction at all its stages and at various temperatures is equal to the sum of the weights of oxidized polymer and volatile reaction products.

In order to clarify the dependence of oxidation speed on temperature, the

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Issledovaniya v Oblasti Vysokomolekulyarnykh Soedinenii, Doklady k 6-oi Konf. po Vysokomolekul. Soedineniyam*, 1949, pages 117–128.

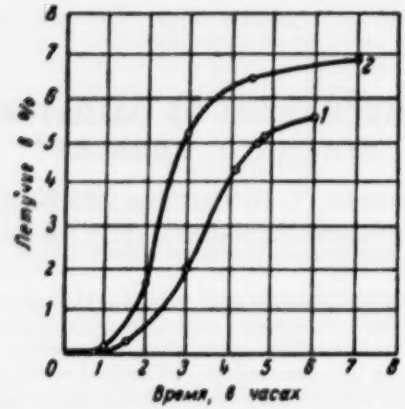


FIG. 1.—Kinetics of the evolution of volatile reaction products in the process of oxidation of the polymer. 1—90° C; 2—100°. The abscissa represents the time of oxidation in hours; the ordinate the per cent by weight of volatile matter, calculated on the sum of the weights of oxidized polymer and volatile matter.

reaction was studied at 80°, 90° and 100° C. Results of the experiment are given in Figure 2.

Without going into a detailed description of the kinetic curves such as we have given earlier[6], we may confine ourselves to the area of retardation of the reaction, where the speed of oxidation gradually declines to small values, even though the number of double bonds consumed does not exceed 50 per cent of the

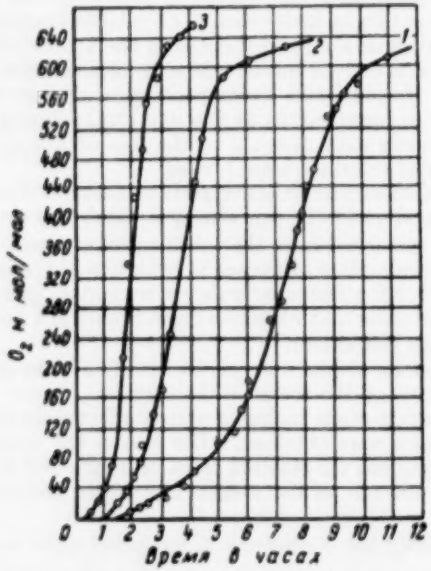


FIG. 2.—Oxidation of the polymer at various temperatures. 1—Experiment No. 22 at 80° C; 2—Experiment No. 21 at 90°; 3—Experiment No. 13 at 100°. The abscissa represents time of oxidation in hours; the ordinate the oxygen absorption in millimoles per mole of polymer.

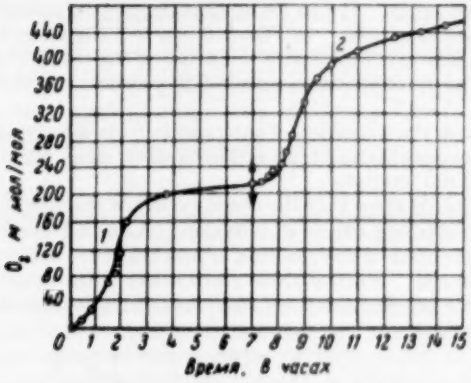


FIG. 3.—Oxidization of the completely oxidized polymer (ground into a powder). 1—Curve of oxidation of the original polymer (thickness of the strip, 160μ); 2—Curve of oxidation of the completely oxidized polymer after grinding to a powder. The abscissa represents time of oxidation in hours; the ordinate the oxygen absorption in millimoles per mole of polymer. The arrow indicates the point at which the polymer was ground up.

original content. It may be assumed that the retardation of the reaction depends on the inhibiting effects of diffusion. In order to convince ourselves of the correctness of such a presumption, we carried out the following experiments: we subjected strips of polymer, 30 and 160μ thick, to oxidation; after the absorption of oxygen ceased, the strips were ground into a powder, which

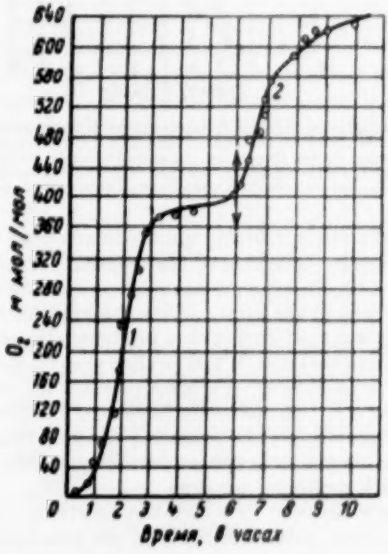


FIG. 4.—Effect of benzoyl peroxide on the oxidation of the completely oxidized polymer. 1—Curve of oxidation of the original polymer; 2—Curve of oxidation of the polymer after grinding into powder and activating with benzoyl peroxide (at the point indicated by the arrow). The abscissa represents time of oxidation in hours; the ordinate the oxygen absorption in millimoles per mole of polymer.

was then oxidized again. It was found that the powder made from thick strips was being oxidized intensely. In Figure 3, curve *1* characterizes the oxidation of thick strips. The arrow indicates the point on the curve where the strip was removed from the reaction vessel, ground to powder, and again subjected to oxidation.

Curve *2* depicts the oxidation of the powder from a fully oxidized polymer. However, the powder obtained from a thin oxidized strip, when again subjected to oxidation, did not oxidize.

These experiments show that the cessation of the reaction in thin strips does not involve the retarding effects of diffusion. A second assumption as to the reason for the inhibition of the reaction is that there are heterodynamic double bonds in the ploymer. Part of these react easily with oxygen, while another part of the double bonds depend on auxiliary activation for their stimulation.

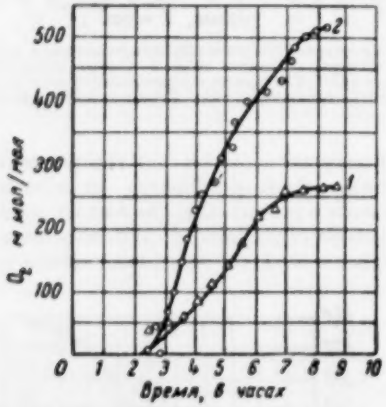


FIG. 5.—Influence of the ratio between double bonds contained in the principal chains of the polymer and those in side chains on the kinetics of oxidation of the polymer. 1—Curve of oxidation of a butadiene polymer whose principal chains contain 20 per cent of the double bonds; 2—Curve of oxidation of a butadiene polymer whose principal chains contain 80 per cent of the double bonds. The abscissa represents the time of oxidation in hours; the ordinate the oxygen absorption in millimoles per mole of polymer.

The exhaustion of the easily reacting double bonds may thus bring about inhibition and the complete cessation of the reaction. In order to confirm this hypothesis, the following experiment was carried out. A thin strip of polymer (30μ thick) was oxidized to the limit. Then the oxidized strip was ground into a fine powder, which was then swelled in a benzene solution of benzoyl peroxide for 24 hours at room temperature. The swollen powder was dried in a vacuum and then subjected to oxidation. Figure 4 presents the curve of oxidation for the original polymer (*1*). At the point indicated by the arrow, the reaction ceased. Curve *2* characterizes the oxidation of the powder. As the diagram shows, benzoyl peroxide makes possible a further oxidation of the "completely" oxidized polymer with molecular oxygen.

In order to clarify the way in which the surviving double bonds are distributed, in fully oxidized polymers, between the principal chains and the side chains, experiments in ozonization were conducted on the polymers.

The loss of unsaturation in the side chains, determined from the ozonolysis data[7], in conjunction with measurement of the total loss of unsaturation, shows

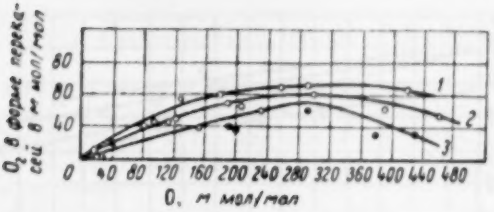


FIG. 6.—Accumulation of peroxides in the process of oxidation of the polymer at various temperatures. 1—80° C; 2—90°; 3—100°. The abscissa represents the absorption of oxygen in millimoles per mole of polymer; the ordinate the amount of oxygen present in the peroxide form, in millimoles per mole of polymer.

that the double bonds in the butadiene polymers have differing reaction capabilities. Thus, in a polymer completely oxidized at 90°, the double bonds in the principal chains were consumed in the amount of 68 per cent, while in the side chains only 14 per cent were consumed. Hence, on the basis of the previous data, we may conclude that oxidation is preferentially distributed to double bonds in the principal chains. The ozonization was conducted according to the method described in the work of Yakubchik, Vasil'ev, and Zhabina[8].

Data on the heterodynamic nature of the double bonds of the principal and side chains makes it possible to surmise that the kinetics of oxidation in butadiene polymers depends to a considerable degree on the proportion between these and other bonds. In order to verify this hypothesis, experiments were set up for oxidation of polymers which differed in the double-bond content of their principal chains. Figure 5 presents the kinetic curves of the oxidation of these polymers[9].

An increase of the double-bond content of the principal chains, as one might expect, leads to an increase of the speed of reaction and a sharp increase of the total oxygen consumption.

Numerous experiments that we conducted[6] showed that the speed of oxidation depends in large degree on the accumulation of peroxide compounds in the system. In Figure 6 curves of the accumulation of peroxides at various tem-

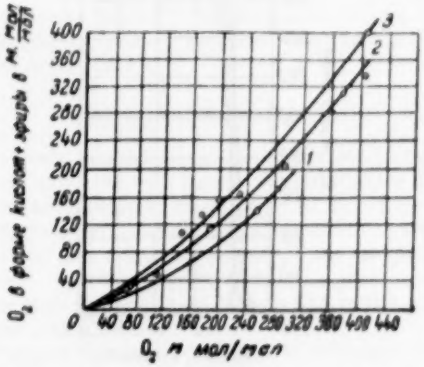


FIG. 7.—Accumulation of carboxylic acids and esters in the process of oxidation of the polymer at various temperatures (solid phase). 1—80° C; 2—90°; 3—100°. The abscissa represents the oxygen absorption in millimoles per mole of polymer; the ordinate oxygen in the form of acids and esters, in millimoles per mole of polymer.

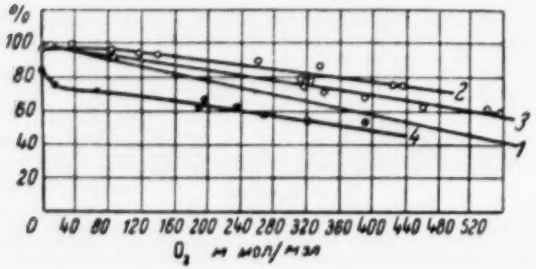


FIG. 8.—Decrease of unsaturation in the process of oxidation of the polymer. 1—Decrease of unsaturation, theoretical curve obtained by calculation from the combination of one molecule of oxygen with a double bond; 2—Decrease of unsaturation at 80° C; 3—The same at 90°; 4—The same at 100°. The abscissa represents absorption of oxygen in millimoles per mole of polymer; the ordinate the per cent unsaturation.

peratures are shown. Curves representing change of peroxide concentration go through a maximum which corresponds in time to the point of inflection in the S-shaped curve of oxygen versus time; i.e., the point at which the speed of oxidation is at its highest. With a rise of temperature, the concentration of peroxide corresponding to a given quantity of combined oxygen decreases.

Among the products of polymer oxidation, no compound with carbonyl groups was detected.

Figure 7 presents curves of the accumulation of carboxyl groups versus the oxidation time. The acids appear at the very beginning of the reaction, and their quantity rises continuously along with the progress of the reaction. In polymer oxidation, a small amount of esterification of carboxyl groups is also found.

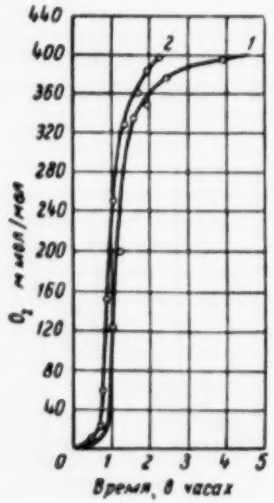


FIG. 9.—Effect of heat treatment on the oxidation of the polymer at 100° C. 1—Curve of oxidation of the polymer; 2—Curve of oxidation of the polymer after heat treatment in a high vacuum at 100° for 4 hours. The abscissa represents time of oxidation in hours; the ordinate the absorption of oxygen in millimoles per mole of polymer.

As already noted[6], oxidation of polymers accompanies a reduction in their unsaturation. Figure 8 shows curves of the loss of unsaturation in the oxidation process.

It can be seen in the diagram that, at temperatures of 80° and 90° C, the loss of unsaturation, determined by analytical means, lags behind that calculated from the combined oxygen. In the early stages of oxidation, in fact, no losses of unsaturation could be detected at all. Farmer found the same situation in natural rubber oxidation.

At the start of oxidation at 100° C, the unsaturation drops faster, and the loss here, determined experimentally, considerably outstrips the loss as calculated. In the range of oxygen absorption from 50 to 520 millimoles/mole at all temperatures, the linear relation between quantitative absorption of oxygen and loss of unsaturation is maintained. For one lost double bond, approximately one molecule of oxygen is expended; as the reaction proceeds, the amount of molecular oxygen going into a double bond increases somewhat.

We showed that, at a temperature near 100°, besides the loss of unsaturation which is immediately connected with oxygen combination, an additional loss of unsaturation takes place in the side chains of the polymer. Along with this, the physical properties of the polymer change considerably. Its solubility in organic solvents sharply decreases, and its tensile strength rises.

All these changes in the polymer indicate the development of the polymerization reaction and the appearance of a three-dimensional structure. If oxidation takes place mainly on the double bonds of the principal chains, and polymerization proceeds mainly in the double bonds of the side chains, one would expect these processes to be somewhat independent of each other.

Actually, as was shown above, the degree of polymerization does not affect the depth of oxidation. However, the question of the influence of polymerization on the character of kinetic curves of oxidation remained unanswered. In order to get a direct answer to the above question, the following experiment was set up: strips of polymer were heat-treated under a high vacuum in the reaction vessel before oxidation. The temperature (100° C) and time of the heat-treatment were the same as for the oxidation. Then the reaction vessel was filled with oxygen and the oxidation took place. In Figure 9, the results of the experiment are given. The curve of oxidation of the heat-treated polymer almost exactly duplicates the curve corresponding to the normal processes of oxidation. Consequently, it may be stated that preliminary polymerization does not affect the oxidation.

DISCUSSION OF RESULTS

The results presented in the experimental portion show that the oxidation speed of a polymer increases with time. The increase is found to be directly connected with the accumulation of stable peroxide compounds in the system. As our earlier experiments[10] showed, the introduction of benzoyl peroxide into the polymer shortens the induction period of the reaction and increases its speed considerably.

In conjunction with the oxidative degradation of the polymer, polymerization also takes place, as was shown earlier.

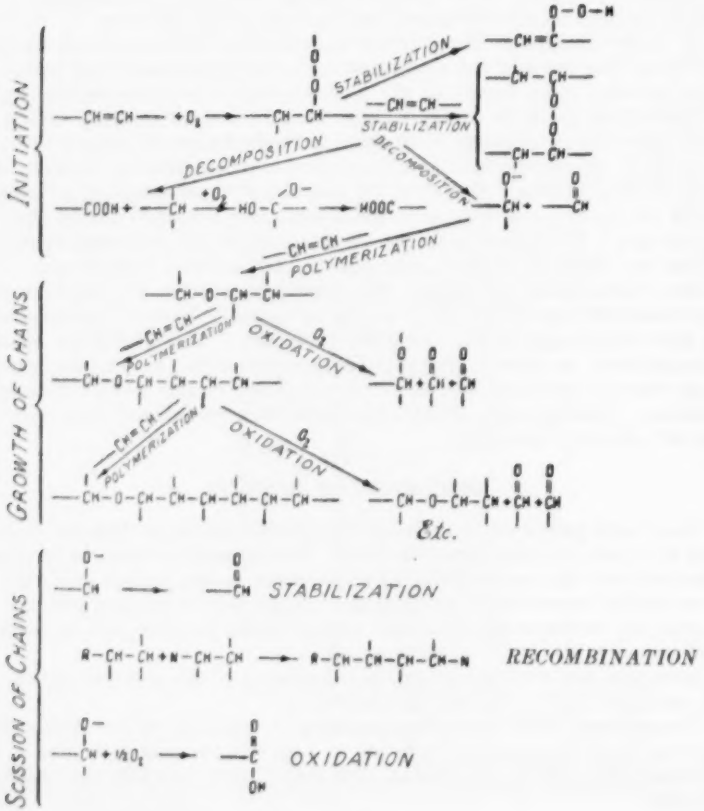
Temperature affects these two reactions in different ways. Although the oxidation has a temperature coefficient of 1.80, still the polymerization at temperatures below 100° C proceeds at a low speed, while near 100° the speed rises markedly.

Such a difference between the effects of temperature on polymerization and on oxidation depends on the specific course of these reactions between long-chain molecules.

According to the diagram adopted by us, oxidation develops as a result of the reaction of the aldehyde radical with oxygen, while polymerization results from the reaction of this radical with the double bond. Both of these reactions proceed for the most part with the same activation energy, which equals 5–6 calories. Thus the difference in speeds cannot be explained by a difference in the activation energy.

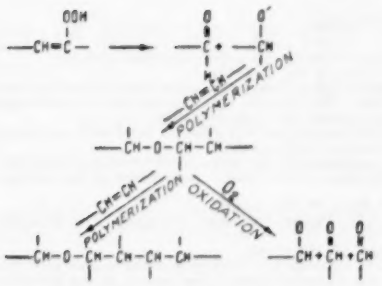
The speed of reaction is determined, not only by the speed of activation, but by the number of collisions. Even though the number of collisions depends little on temperature, since a molecule of gas is reacting with a chain molecule; still, in polymerization (where the reaction takes place between two chain molecules) the temperature will have a strong effect on the mobility of the chains and, therefore, on the number of their collisions.

OXIDATION DIAGRAM OF THE SODIUM-BUTADIENE POLYMER
PRIMARY CHAIN



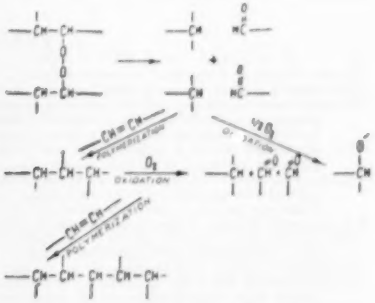
SECONDARY CHAIN:

Variant I



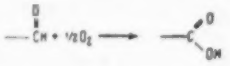
and so forth, according to the primary chain diagram.

Variant II



and so forth, according to the primary chain diagram.

The secondary reaction:



The diagram supplied above represents the general mechanism of oxidation, as including two reaction routes: oxidative decomposition and polymerization.

The initiation of primary chains takes place when oxygen reacts directly with the double bonds of the polymer molecules. However, the secondary chains are initiated at the expense of energy liberated by the decomposition of stable peroxides. Both the primary and the secondary chains develop by way of the very same intermediate active centers of the radical type.

Scission of the chains takes place as a result of recombination, but also as a result of stabilization or oxidation of aldehyde radicals. The scission of chains, as the diagram shows, leads to the growth of a three-dimensional structure.

SUMMARY

1. Adequately reproducible results were obtained, and a complete balance was achieved between substances entering the reaction and the products of oxidation.

2. It is shown that the oxygen which enters into the reaction at all stages of oxidation is retained mainly in the form of peroxides, acids, and ethers.

3. The kinetics of polymer oxidation, and also the accumulation of intermediate reaction products, were studied at various temperatures.

4. It is shown that the cessation of oxidation occurs long before the exhaustion of the polymer's double bonds; the reasons for this phenomenon are revealed.

5. The decrease of unsaturation in the process of oxidation at different temperatures was studied.

6. It is shown that the process of oxidative decomposition is accompanied by polymerization.

7. It is shown that oxidation extends mainly to the double bonds in the principal chains, while polymerization is confined mainly to the double bonds in the side chains.

8. A diagram of the oxidative mechanism is given, including both of the directions of reaction (decomposition and polymerization).

REFERENCES

[1] In the remainder of the text, the word *polymer* is understood to mean a sodium-butadiene polymer.
[2] Kuzminskii, Shanin, Degteva, and Lapteva, *Kolloid. Zhur.* **9**, No. 5 (1947).
[3] *Volatile matter* is what we call the products of oxidation which are converted, under the experimental conditions, from a solid polymer phase to a gaseous one. The quantity of this is calculated in percentage by weight, based on the total weight of oxidized polymer plus volatile matter.
[4] The calculation of loss of unsaturation was made on the assumption that a double bond under oxidation gives one molecule of volatile matter (formaldehyde or formic acid).
[5] Here, as below, all calculations of molecular oxygen combined with the polymer are based on a structural unit of the original polymer containing one aliphatic double bond. In the case of the sodium-butadiene polymer, one mole equals 54 grams.
[6] Kuzminskii, Shanin, Degteva, and Lapteva, *Kolloid. Zhur.* **10**, No. 1 (1948).
[7] The ozonolysis was carried out by R. M. Belitskaya in the Physico-Chemical Laboratory of the Scientific Research Institute of the Rubber Industry.
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CHAIN SCISSION IN THE OXIDATION OF HEVEA.* I.

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INTRODUCTION

The essential role of oxygen in the reduction of viscosity of unvulcanized rubber during mastication is well known in a qualitative way, but there is little quantitative information about the efficiency with which it is used in this process. A recent study of the low-temperature breakdown of Hevea by Pike and Watson[1] clearly suggests that the efficiency (measured in terms of scissions of the hydrocarbon chain per mole of oxygen absorbed) is high under conditions where mechanical rupture of carbon to carbon bonds is important. At elevated temperatures (above about 120°), the viscosity of Hevea has fallen sufficiently so that mechanical rupture is no longer effective, and mastication serves only to mix the rubber and to expose continuously fresh surfaces to air. Measurements of the efficiency of oxidation on films thin enough so that oxygen diffusion does not affect the results should, therefore, be satisfactory to determine the efficiency of oxidative scission under practical milling conditions.

It is not possible to make such measurements with ordinary forms of rubber without some preliminary degradation of the hydrocarbon, either accompanying solution in a solvent or during milling to produce a thin sheet. The USF rubber process[2] affords a particularly convenient source of undegraded rubber, which has been used in this investigation.

EXPERIMENTAL

USF type rubber was prepared by a slight modification of the published procedure[2]. Normal latex, preserved with 0.4% formaldehyde by weight, was diluted with distilled water to give a calculated ash content in the final rubber equal to that of commercial USF. After adjustment of the pH to 3.8 to 4.0 with formic acid, the mixture was allowed to cream for 24 hours. The cream was separated from the clear serum and spread on glass to give a final film of the desired thickness after drying. All the films were less than 0.01 cm. thick. Films were wrapped in desized glass cloth for oxidation.

Oxidations were carried out at a constant pressure of one atmosphere of oxygen, in a simple apparatus consisting of a large test-tube mounted in a circulating air oven. The test-tube was connected by capillary glass tubing to a reference manometer and a manually operated gas buret maintained at 30°. The reference manometers were connected to a reservoir of air at constant temperature to eliminate the effect of variations in atmospheric pressure. Lumps of barium oxide were mounted in the oxidation cells during an experiment to absorb evolved water and acid.

Cells containing the samples were evacuated with a mechanical pump, allowed to reach the oven temperature, then filled with oxygen preheated to the operating temperature. Oxygen consumed was measured with the gas buret

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by periodic adjustment to the reference pressure. During an experiment samples were removed from the oven after the desired amount of oxygen had been absorbed and cooled rapidly to room temperature. Intrinsic viscosities of the oxidized rubbers were determined in benzene solution.

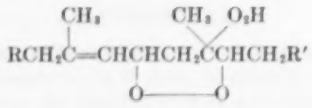
Molecular weights were calculated from the relationship between intrinsic viscosity and number average molecular weight reported by Carter, Scott and Magat[3]. Use of this relation involves the implicit assumption that the ratio of number average to viscosity average molecular weight does not change materially during oxidation.

DISCUSSION

Results of one experiment are shown in Table I and results of measurements at three temperatures in Table II.

Published estimates of the efficiency of chain scission during oxidation of raw Hevea have been based largely on experiments at low temperature, where oxidative scission may be expected to be relatively inefficient[4]. Tobolsky, Metz and Mesrobian[5] have shown that the efficiency of scission should, and does, increase as the rate of oxidation increases, as has also been found here. The measurements of Tobolsky and coworkers were made with vulcanized rubbers; they observed a higher limiting efficiency than was found for raw Hevea in this work. When oxidation was carried out at the maximum rate at a given temperature, very nearly one scission of the hydrocarbon per mole of oxygen absorbed chain was found.

The only published work which affords a guide for an attempt to formulate a reaction scheme which would explain the observed efficiencies is that of Bolland and Hughes[6] on the primary oxidation product of squalene, a low molecular weight model for rubber. They have shown that this hydroperoxide contains four atoms of oxygen, and suggest that the structure which predominates in the product is of the form:



Investigation of the oxidation of rubber in latex[7] has given evidence that one isoprene unit is destroyed for every chain scission. If it is assumed that the Hevea hydroperoxide has the same structure as that found for squalene, a plausible reaction sequence may be envisioned, which yields the observed low molecular weight products of the scission reaction: carbon dioxide, acetic acid,

TABLE I

OXIDATION OF USF RUBBER AT 130°

Time in oven (min.)	Oxygen absorbed (mmoles/ 100 g.)	Gel (%)	[η]	Moles oxygen / Moles scissions
—	0	7	9.08	—
10	1.06	4	2.88	5.6
30	2.50	6	2.82	12.5
40	3.47	3	2.21	11.3
48	4.25	8	1.94	10.8
68	6.36	6	1.60	12.2
				Mean 10.5

TABLE II

EFFICIENCY OF CHAIN SCISSION BY OXYGEN

Temp. (° C)	130	130	130	140	150
Moles oxygen / Moles scissions	10.5	11.4	11.3	6.2	6.3

and formic acid. This scheme requires six moles of oxygen per mole of chain scissions, which is close to the amount observed in the present work at the higher temperatures.

If the interpretation of hydrocarbon scission given here and in the following paper[7] is correct, some alternative or additional mechanism must exist to give the high efficiencies observed by Tobolsky, Metz, and Mesrobian. Since the reaction of oxygen with the rubber hydrocarbon itself would not be expected to be greatly modified by oxidation under low stress, an obvious possibility exists that direct attack at the points of cross-linking is important in the vulcanized rubber.[8]

SUMMARY

The efficiency of chain scission of raw Hevea by molecular oxygen increases rapidly with increase of temperature to a limiting value of about 6.2 molecules of oxygen per bond broken. This value is close to the theoretical for destruction of one isoprene unit per bond broken, which leads to the inference that the higher efficiencies which have been reported for oxidation of vulcanized rubber may be the result of scission at the points of cross-linking.

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[8] It has been pointed out that this discussion ignores the effect of possible cross-linking during oxidation. There is, at present, no published evidence which would permit a satisfactory estimate of the importance of a cross-linking reaction during the oxidation of Hevea. It is well known that oxidized rubber becomes cross-linked in the absence of oxygen and that vulcanizates become reinified on severe oxidation, but the nature of these changes is undetermined. Using a disazodicarboxylate as the curing agent, Metz and Mesrobian (*J. Polymer Sci.*, 11, 83 (1953)) have determined the change in modulus of well characterized simple Hevea vulcanizates when oxidized, both relaxed and under stress. As nearly as can be estimated from their data, presented graphically, scission efficiency was the same within experimental error, whether calculated from stress relaxation or modulus change, up to about 8 hours (at 80°). At this time the samples had absorbed roughly 100 millimoles of oxygen per hundred grams, most of which is involved in reactions other than scission. This is about ten times the maximum amount absorbed by the rubber in the experiments reported here. It is probable that oxygen-induced cross-linking occurs through secondary reactions which, in Hevea, are suppressed at high oxygen concentrations, unless so much oxygen has been combined with the rubber that substantial changes in the hydrocarbon have occurred.

II.

INTRODUCTION

Establishment of the structure of the product formed from cyclohexene by reaction with oxygen[1] initiated a period of increasingly intensive investigation of the interaction of olefins with molecular oxygen, which has now reached the stage where it has been described[2] as "one of the most thoroughly understood chemical processes". One general reaction scheme, modified in detail to account for variations in substrate structure, explains the observed features of hydrocarbon autoöxidation in a very satisfactory manner: oxidation of all

compounds having the necessary hydrogen adjacent to the (isolated) unsaturation leads to an α-hydroperoxide as primary product.

The subsequent fate, on continued oxidation, of the peroxide formed initially is less thoroughly understood, except for a few relatively simple compounds whose hydroperoxides decompose smoothly by clear reaction paths[3]. The sequence of steps leading to scission of carbon to carbon bonds, of special technological importance in the oxidation of rubber, has remained obscure. For this hydrocarbon, in fact, the considerable experimental difficulties encountered have prevented a direct demonstration of the nature of its initial oxidation product, although the work of Bolland[4] with model compounds leaves little doubt as to its structure.

Further progress in the understanding of this reaction now requires a knowledge of the identity and relative amounts of the products formed when the peroxide decomposes. It has been known for over forty years that volatile products are associated with the oxidation of rubber[5], being evolved from the beginning of the reaction. Water, carbon dioxide[6], and formic acid[7] have been identified among these. In the earliest work, volatile materials were usually dismissed as resulting from minor side reactions or from oxidation of nonrubber components, although Dawson and Porritt obtained an estimate of the molecular weight of balata, based on the yield of formic acid obtained by oxidizing it, which was nearly of the right order of magnitude. More recently, volatile compounds have been recognized as real products of the oxidation reaction, although they have not been quantitatively correlated with hydrocarbon degradation: the yields of water and carbon dioxide, for example, were characterized by Farmer and Sundralingam[8] as "small but not negligible".

It has been known for some time that oxidation of latex at low temperature results in the formation of acid[9]. When this was reinvestigated at higher temperatures to obtain reasonable rates of oxidation, the yields of acid were found to be surprisingly high. The results reported here were obtained by further study of this phenomenon.

Although it is possible to measure volatile products of the oxidation of solid rubber or of rubber in solution quantitatively, some of the experimental difficulties can be avoided by carrying out the reaction in latex: the rubber is highly concentrated, yet finely dispersed, so that large samples may be used to obtain adequate yields of oxidation products, without the intrusion of oxygen diffusion effects, and the latex remains stable over a wide range of extents of oxidation so that handling the oxidized rubber is not a problem.

Rigorous purification is not required to obtain reproducible results with latex. The rate of oxidation is constant[9] and much higher than the initial rate of oxidation of dry rubber from the same latex. It is apparently determined by traces of metals, particularly copper, the rate-controlling step involving transfer of metal ions between the two phases. Experiments not reported here have shown the efficiency of scission by oxygen and the yields of volatile products are not affected by changes in copper concentration.

EXPERIMENTAL

The latex used in this work was a commercial creamed latex (United States Rubber Co.), preserved with ammonia, which contained 67 to 68.5% total solids in the samples used.

Oxidation experiments were made with a simple apparatus in which reaction cells consisting of 200-ml. round-bottom flasks were connected to a reservoir of

oxygen at the reaction temperature (90°) and through flexible capillary connections to mercury manometers at room temperature. The flasks were mounted on a "Wrist-Action" shaker (Burrell Technical Supply Co.) oscillating at about 240 cycles per minute. Frothing of the latex provides intimate mixing of gas and liquid, so that the extremely vigorous agitation required for oxidation of pure organic liquids[10] was not found necessary here.

Oxidations were carried out at a total pressure of about 1.8 atmospheres, the amount of oxygen consumed being calculated from the pressure drop in the cells. This arrangement, although capable of less precision than measurements at constant pressure, is considerably more convenient experimentally and yields

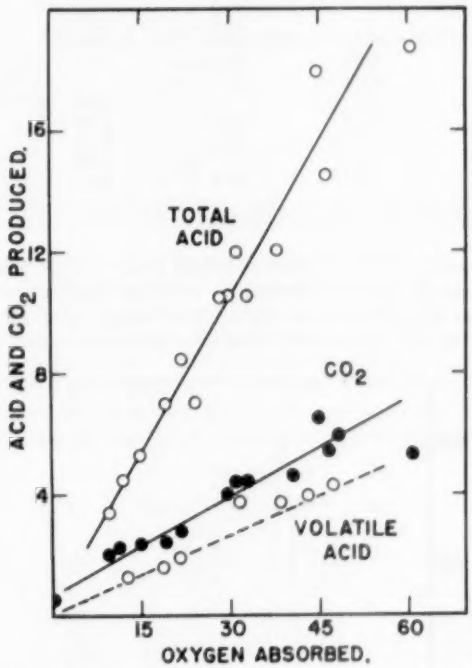


FIG. 1.—Acid and CO_2 produced as a function of oxygen consumed: acids in meq./100 g. latex solids, carbon dioxide and oxygen in mmoles/100 g.

rates of oxidation reproducible within less than 5%. The rates observed were independent of oxygen pressure over a wide range, and became erratic only when substantial changes in the latex had occurred.

After a sample had absorbed the desired amount of oxygen, it was removed from the bath and cooled rapidly to room temperature. Samples of rubber for viscosity determination were obtained by drying aliquots at room temperature. Further oxidation during the drying process was negligible. Viscosities were determined in chloroform solution in Ostwald viscometers and molecular weights calculated from the relation of Carter, Scott and Magat[11], applying a correction for the 10% higher intrinsic viscosity in chloroform.

Total "titratable acids" were determined by potentiometric titration of an

TABLE I

TOTAL ACID AND CARBON DIOXIDE PRODUCED

Oxygen[a] absorbed	Final pH	NaOH[a] titer	CO_2[a] found	CO_2 titer[a] calcd.
0	10.00	11.9	1.31	—
0[b]	10.08	11.0	1.06	—
9.9	10.12	15.3	3.26	3.3
12.0	9.90	16.4	3.49	3.8
15.0	9.72	17.2	3.62	4.2
19.0	9.67	18.9	3.66	4.4
22.0	9.48	20.4	4.01	5.2
24.1	9.50	18.9	—	—
28.4	9.40	22.4	—	—
29.8[b]	—	21.5	5.07	7.8
31.0	9.45	23.9	5.66	8.5
33.0	9.25	22.4	5.71	8.4
37.7	9.30	23.9	—	—
40.3[b]	—	—	5.62	9.1
44.7	9.10	29.8	7.84	13.9
46.6[b]	—	25.5	6.47	10.8
48.1[b]	—	—	5.96	11.0
60.7	8.90	30.6	6.59	10.6

[a] Oxygen and CO_2 in mmoles/100 g. latex solids, NaOH and CO_2 titers in meq./100 g.
[b] Samples designated thus from a different lot of latex.

aliquot of the latex with 0.1 *N* NaOH to pH 11.2. (This is a measure of the sum of ammonium ion and bicarbonate.) Carbon dioxide was determined by passing a stream of CO_2-free air through a second aliquot, stabilized with Emulphor-ON (General Dyestuff Corporation) and made acid with phosphoric

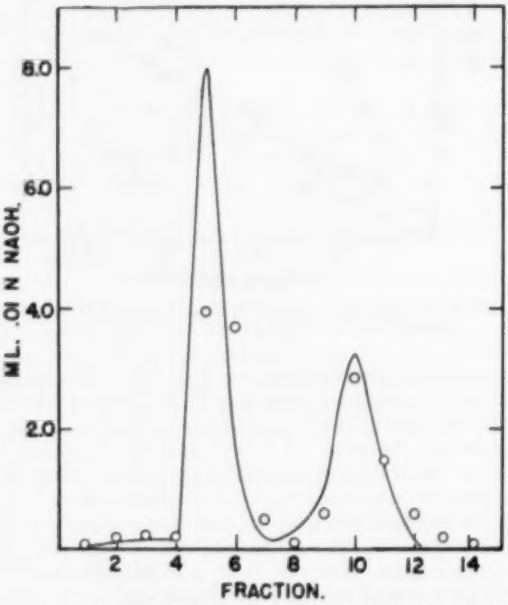


FIG. 2.—Separation of volatile acids: circles, mixture obtained from latex; solid line, known mixture of acetic (first peak) and formic acids.

acid, collecting it in Ascarite, and weighing. Volatile acid other than CO_2 was determined essentially by the micro-method of Philpott and Sekar[13], using sulfuric acid to coagulate the latex.

The yields of total titratable acid, carbon dioxide, and volatile acid from a series of oxidations are plotted in Figure 1. In order to determine if all titratable acid was accounted for, the amounts of alkali required to titrate the carbon dioxide formed were calculated (Table I) and plotted against the actual titer. A line through these points had a slope of 0.75. Since the volatile acid is very close to one-fourth the total titer (dashed line of Figure 1), no other acid was formed, within the experimental error.

TABLE II

VOLATILE ACID PRODUCED DURING OXIDATION

Oxygen absorbed (mmoles/ 100 g. TS)	Volatile acid[a] (meq./ 100 g. TS)	Oxygen absorbed (mmoles/ 100 g. TS)	Volatile acid[a] (meq./ 100 g. TS)
12.8	1.24	38.4	3.72
18.8	1.60	43.2	3.95
21.6	1.96	47.5	4.29
32.0	3.78		

[a] Corrected for blank, 0.45 meq./100 g. TS.

A pooled sample of serum from the aliquots used for determination of volatile acid was distilled to recover sufficient material for identification. Preliminary examination of a portion of this on a silica column containing bromocresol green as indicator[12] gave no evidence of the presence of acids of higher molecular weight than acetic. Elution with 5% *n*-butanol in chloroform yielded two approximately equal fractions, the first of which had the mobility of acetic acid. Another portion was then separated quantitatively on a silica column in which the fixed phase was 0.5 *N* sulfuric acid[14], using 7.5% *t*-amyl alcohol in

TABLE III

CHAIN SCISSION BY OXYGEN

Oxygen absorbed (mmoles/ 100 g. T.S.)	$[\eta]$ (in $CHCl_3$)	Chain scissions (mmoles/ 100 g. T.S.)	Oxygen absorbed (mmoles/ 100 g. T.S.)	$[\eta]$ (in $CHCl_3$)	Chain scissions (mmoles/ 100 g. T.S.)
0	5.65	0	6.8	2.33	0.28
1.4	3.94	0.077	7.1	2.22	.30
2.3	3.68	.090	8.5	1.91	.40
2.9	3.35	.12	11.3	1.63	.54
3.5	3.22	.13	14.5	1.39	.70
4.8	2.65	.21	38.7	0.73	2.05
5.5	2.65	.21			

chloroform as eluent, and titrating 5-ml. fractions with 0.01 *N* NaOH. The result of this separation is compared in Figure 2 with that of a known mixture of 0.8 meq. of acetic acid with 0.5 of formic. From the figure the fraction of formic acid in the unknown mixture is 41.5%. When a separate sample was oxidized with mercuric chloride[15], the formic acid found was 42.5%.

The pooled sera used as starting material contained an average of 12 μeq. per gram. Assuming that acetic and formic acids are produced in equivalent amounts during oxidation, and correcting for acetic acid already present in the oxidized latex (1.4 μeq. per gram of serum), the calculated fraction of formic acid is 44%.

RESULTS

The results of the determination of scission efficiency, total acid, carbon dioxide, and other volatile acid as a function of oxygen consumed by the latex are given in Tables I through III[16] and plotted in part in Figures 1 and 3, with appropriate corrections for amounts originally present. The curve for CO_2 does not pass through the origin because some carbon dioxide (about 0.5 meq./100 g. latex solids) is evolved on heating in the absence of oxygen.

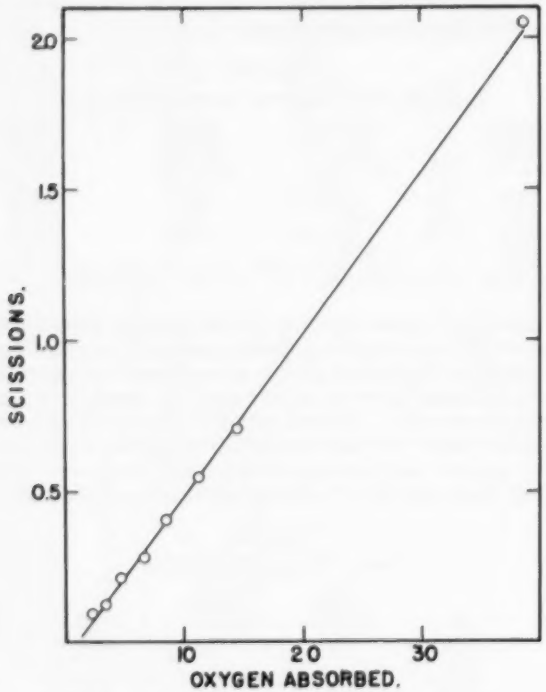


FIG. 3.—Chain scissions as a function of oxygen absorbed, both in mmoles/100 g. latex solids.

Each of these quantities is a linear function of oxygen absorbed within experimental error. The slopes of the plots of scissions, CO_2 and volatile acid as a function of oxygen are: scissions/O_2 = 0.054 mole/mole; CO_2/O_2 = 0.108 mole/mole; acid/O_2 = 0.095 eq./mole.

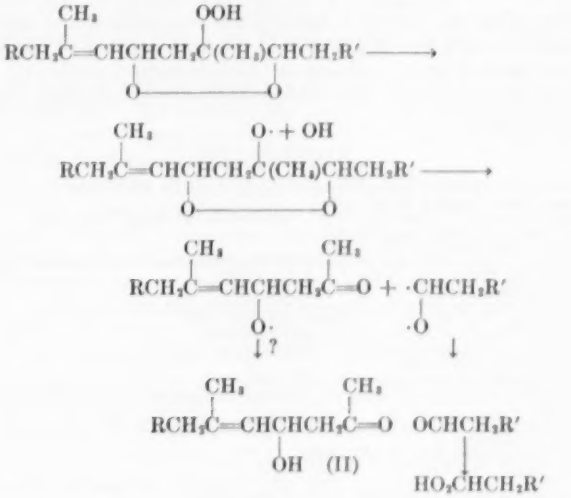
From these quantities the ratios of acids to scissions may be calculated: CO_2/scissions = 2.02 moles/mole; acid/scissions = 1.75 eq./mole.

DISCUSSION

Knowing that the volatile acid consists of equal amounts of acetic and formic, we have to account for the production of two molecules of carbon dioxide, one of acetic, and one of formic acid for every scission of the hydrocarbon chain. This can be accomplished in a reasonably satisfactory manner if it is

assumed that the primary oxidation product of rubber is a cyclic diperoxide having the structure indicated by the results of the work of Bolland and Hughes[4] with low molecular weight polyisoprenes. (It may be noted here that squalene, oxidized under the conditions used in this work, gives yields of total acid and of carbon dioxide close to those found for rubber.)

The initial product I is a tertiary hydroperoxide which is assumed to undergo total oxidative destruction following dissociation of the hydroperoxide group:



(I)

In the absence of any information about the oxidation of compounds of the structure (II), we can only speculate on the details of its further oxidation, rapid compared with attack on the hydrocarbon itself. Assuming stepwise degradation from the terminal methyl ketone, the final products, arranged in the same order as the carbon atoms of formula II above, will be

$$RCH_2\underset{\underset{O}{\|}}{C}CH_3 + HCO_2H + 2CO_2 + CH_3CO_2H + H_2O$$

The scheme outlined here is consistent with all known features of the reaction. The postulated end groups on the severed hydrocarbon chains are in reasonable agreement with published analyses[17] of highly oxidized Hevea, and the known rapid oxidation of aldehydes at the temperature used here[15]. The yields of volatile materials are in the proportions found by experiment. The scheme requires six molecules of oxygen for each scission of the hydrocarbon chain, in good agreement with the limiting value found on rapid oxidation of dry rubber at high temperatures[16].

The total amount of oxygen consumed (18.5 moles/mole of scissions) at the temperature of these experiments is much larger than that required for the scission reaction. Most of the additional oxygen appears in hydroxyl[17] and, probably, ether[18] groups. It is not clear whether the ratio of oxygen required for scission to the total is a measure of the relative amount of hydroperoxide having the structure assumed by Bolland and Hughes to predominate, or if this

structure decomposes by alternate paths of which only one involves thermal scission of the tertiary alkoxy group with consequent scission of the hydrocarbon as a whole. In view of the good agreement between the postulated mechanism and the oxygen requirements at high temperature and of the decreasing yield of scission as the temperature is lowered[19], the second alternative may be correct.

SUMMARY

Oxidation of natural rubber in latex yields two molecules of carbon dioxide, one of formic acid and one of acetic acid for each rupture of the hydrocarbon chain. The yields of these products can be interpreted readily by reference to the structure of the primary oxidation products of 1,5-diolefins established by Bolland and Hughes.[4]

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[19] Farmer and Sundralingam, *J. Chem. Soc.* **1943**, 125; Scissions are net scissions. The possibility of the effect of cross-linking is discussed in Part I of this series.

SOME FEATURES OF THE AGING OF VULCANIZED RUBBER IN LIGHT *

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The action of light on rubber articles is almost always accompanied by a rise of their temperature. We may assume also, on the basis of a number of literature data, that there is a still more intimate relationship between the processes of light and the heat aging of vulcanizates.

It is known that the rate of purely photochemical reactions depends but little on temperature. Such a dependence is noticeable, however, in such cases as the following: (1) when photoreactions and thermoreactions develop parallel to, and independently of, one another, their rates being found to be additive; (2) when they have a common level of reaction and common intermediate reaction products, and also when there exists a reciprocal activation of photo- and thermoreactions by one another. In this case, a change of temperature (within known limits) should bring about a change of the rate of photochemical reactions which is greater than the additive change. This has been confirmed by experiments on a number of vulcanizates. Thus, for example, there are data to the effect that the light aging of a natural-rubber vulcanizate[1] is sharply accelerated by an increase of temperature from 25° to 75–100° C, and the same is true of Butyl rubber[2].

We have investigated the heat, light, and heat-light aging of strips, about 100μ thick, of pure vulcanizates of a typical structure-forming rubber, viz., polybutadiene, and of a rubber lacking structure, viz., Butyl rubber. The exposure of the polybutadiene strips to light was carried out in a constant-temperature apparatus at 25° and 80° C, with a mercury-quartz lamp PRK-7, through pyrex glass and a layer of distilled water.

The distance from the center of the lamp to the sample was 15 cm. For a sensitive index of the changes taking place during the aging of the vulcanizates, we chose the ratio between the conditional modulus of elasticity of a strip exposed to light after 30 minutes under stress, and the corresponding modulus of an unexposed strip. The Butyl vulcanizate was tested in an apparatus with a car on wheels, described previously[3]. The strips were irradiated at a distance of 5 cm. by a PRK-2 lamp, through pyrex glass and distilled water, while under continuous stress.

We determined the ratio $a = E'/E_0$ between the conditional modulus of strips exposed to light 30 minutes after the start of the stress, E', and the modulus of the unexposed strips, E_0. To characterize the influence of added ingredients on the light aging of a vulcanizate, we selected the ratio a_1/a_0, where a_1 is the value of a for strips with the additive, and a_0 is the value of a for the original strips. In the case of the destructurizing Butyl rubber, a value $a_1/a_0 > 1$ indicates a protective action on the part of the additive, while a value $a_1/a_0 < 1$ indicates that it has a sensitizing action.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Malcolm Anderson from *Doklady Akademii Nauk SSSR*, Vol. 90, No. 6, pages 1063–1066 (1953).

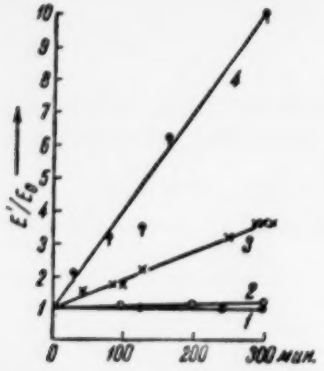

FIG. 1.—The kinetics of the aging of a polybutadiene vulcanizate. *1*—25°, in darkness; *2*—80°, in darkness; *3*—25°, exposed to light; *4*—80°, exposed to light. The abscissa represents time in minutes; the ordinate the ratio of the moduli, E'/E_0.

It can be seen in Figure 1 that at 25° C in the absence of light exposure, the modulus of the strip of polybutadiene vulcanizate remains practically unchanged; at 80° the modulus rises only slowly. When the strips are exposed to light, however, heating to 80° causes a disproportionately large increase of the rate of the process, in comparison with the light aging at 25°. We also observed an analogous disproportionately large increase of the rate of aging of an irradiated Butyl rubber vulcanizate as its temperature was raised from 25° to 60° C.

The above facts attest to the close relation between the processes of light and heat aging of vulcanizates, a relation arising, not only from the conversion of light energy into heat energy, but also from the reciprocal activation of these processes; hence light-heat aging should be considered as a single process.

The relative roles of light and heat in the exposure of vulcanizates to light depend, not only on the intensity of the light and the temperature, but also on the composition of the vulcanizate, with respect to the concentration in it of ingredients which show a strong light absorbance. The introduction into the vulcanizate of substances which strongly absorb light (carbon black, pigments, heat-aging inhibitors) should diminish the relative role of the action of light in

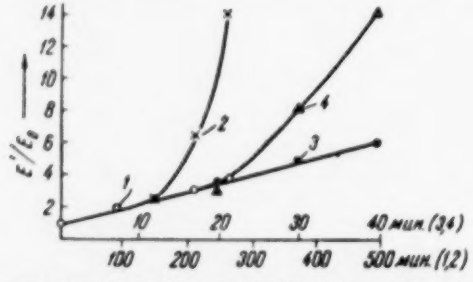

FIG. 2.—The decrease in the photosensitizing action of PBNA in a polybutadiene vulcanizate with a rise of temperature. *1* and *2*—25° C; *3* and *4*—80°; *1* and *3*—without phenyl-2-naphthylamine; *2* and *4*—with 0.93% phenyl-2-naphthylamine. The abscissa scales represent the time in minutes, the top scale applying to curves *3* and *4* and the bottom ones to *1* and *2*; the ordinate represents the ratio of the moduli, E'/E_0.

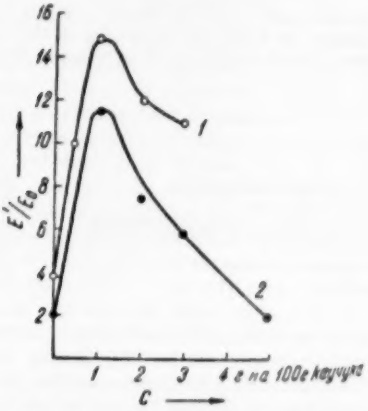

FIG. 3.—The sensitization of a polybutadiene vulcanizate to light with various concentrations of the sensitizer. *1*—Phenyl-2-naphthylamine after 270 minutes' light exposure; *2*—Aldol-1-naphthylamine after 210 minutes' exposure. The abscissa represents the concentration of the sensitizer in grams per 100 grams of rubber; the ordinate the ratio of the moduli, E'/E_0.

comparison with the action of heat[4]; and also a rise of temperature with no change of the light intensity should have the same effect.

In view of the close interrelation between heat and light aging, it was logical that various heat-aging inhibitors (antioxidants), as well as several light-filtering substances, would be adopted as protective agents against heat-light aging. Experimentation conducted on polybutadiene and Butyl vulcanizates showed that a number of excellent heat-aging inhibitors, at ordinary temperatures, also sensitized these vulcanizates to light. For example, phenyl-2-naphthylamine, dinaphthylamine, and *p*-hydroxyphenyl-2-naphthylamine in a concentration of 1 gram per 100 grams of the rubber, sensitized both vulcanizates (see Tables 1 and 2); ketamine, aldol-1-naphthylamine, di-*tert*-butylhydroquinone, and a number of others sensitized the polybutadiene vulcanizate.

A number of light-filtering materials which absorb strongly in the near-ultraviolet region (see Table 1, Nos. 5–9) also turned out to be light-sensitizers

TABLE 1

THE KINETICS OF CHANGE OF THE CONDITIONAL MODULUS OF ELASTICITY OF A SKB-BASED VULCANIZATE DURING ITS SENSITIZATION TO LIGHT

Test No.	Sensitizer	Duration of light exposure in minutes							
		90	150	210	270	290	330	370	410
1	Control (no sensitizer)	2	2.6	3.6	3.6	3.6	—	3.5	6
2	Phenyl-2-naphthylamine, 0.9%	1.5	2.7	6.6	15	—	—	—	—
3	Aldol-1-naphthylamine, 0.9%	1.9	—	1	—	14	—	—	40
4	*p*-Hydroxyphenyl-2-naphthylamine, 1.8%	1.5	—	2.5	3.3	15	—	—	—
5	Phenanthrene, 0.9%	2.5	—	4.6	—	—	5.5	—	6.9
6	Anthracene, 0.9%	3.9	—	7.7	—	12	—	—	—
7	Anthraquinone, 0.9%	4.6	—	—	—	6	—	—	12
8	Dinitrophenol, 0.9%	1.9	1.8	3.2	6.3	—	—	15	—
9	Salol, 0.9%	1.5	—	2.6	—	8.0	—	12	—
10	Ketamine, 0.9%	2.5	3.3	4.7	—	11	—	—	—
11	Di-*tert*-butylhydroquinone, 1.8%	2.6	—	2.6	—	5.0	—	7.5	—
12	Dihydroxydiphenyl	2.0	—	3.5	—	4.5	—	—	—
13	Mercaptobenzimidazole, 0.9%	1.8	—	3.0	—	—	4.5	—	6.5
14	Phenyl-2-naphthylamine, 0.9% plus Sudan black, 0.9%	2.5	—	2.5	—	6	—	—	—
15	Phenyl-2-naphthylamine, 0.9% plus aldol-1-naphthylamine, 0.9%	1.4	—	1.6	—	2.4	—	3.4	—

TABLE 2

THE EFFECT OF VARIOUS ADDITIVES (0.9%) ON THE LIGHT-AGING OF BUTYL VULCANIZATE STRIPS

Test No.	Additive	a_1/a_0 at temperatures 25° C	60° C
0	No additive	1	1
1	Phenyl-2-naphthylamine	0.65	0.85
2	Dinaphthylamine	0.43	—
3	p-Hydroxyphenyl-2-naphthylamine	0.8	1.2
4	Phenanthrene	1.0	1.3
5	Phenylnitromethane	1.0	1.6
6	Ketamine	1.1	1.5

for the polybutadiene vulcanizate. We have already mentioned the sensitizing action of phenyl-2-naphthylamine on polybutadiene, Butyl rubber, a Butyl vulcanizate and polyisobutylene[3]; it is known also that phenyl-2-naphthylamine is a light-oxidation sensitizer for natural rubber as well[5].

In the present work, we have investigated in detail the effect of phenyl-2-naphthylamine on the light aging of vulcanizates: (a) at various temperatures; (b) with various concentrations of phenyl-2-naphthylamine and (c) when light-filtering substances are introduced.

(a). As Figure 2 shows, phenyl-2-naphthylamine in the amount of 1 part by weight per 100 parts of the rubber, has at 25° C a light-sensitizing effect on the polybutadiene vulcanizate. When the temperature is increased to 80°, this sensitizing action decreases with an increase of the relative role of phenyl-2-naphthylamine as a heat-aging inhibitor. In the Butyl vulcanizate, phenyl-2-naphthylamine behaves analogously (Table 2). An even more pronounced temperature effect was noted by us in the light aging of a Butyl vulcanizate containing 0.9 per cent of *p*-hydroxyphenyl-2-naphthylamine. Although at 25° *p*-hydroxyphenyl-2-naphthylamine is a sensitizer, at 60° its action as a heat-aging inhibitor becomes dominant (Table 2).

In the case of phenanthrene, phenylnitromethane and ketamine, likewise, we find that, at 25° C, these substances exert virtually no influence on the light-

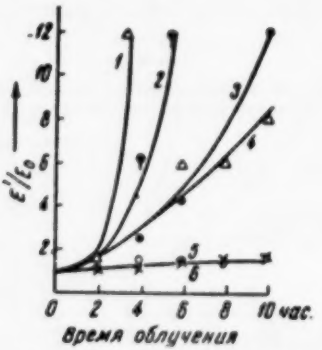

FIG. 4.—The kinetics of the aging of carbon-black-loaded vulcanizates of polybutadiene on exposure to light. *1*, *2* and *6*—Without phenyl-2-naphthylamine; *3*, *4* and *5*—with phenyl-2-naphthylamine; *1* and *3*—3 grams of black per 100 grams of rubber; *2* and *4*—10 grams of black; *5* and *6*—60 grams of black. Temperature—25° C. The abscissa represents the time of exposure in hours; the ordinate the ratio of the moduli, E'/E_0.

aging of the Butyl vulcanizate, whereas at 60° they exhibit a protective action (Table 2).

(b). When the concentration of phenyl-2-naphthylamine is increased, its sensitizing action passes through a maximum (Figure 3). The subsequent drop in this action of phenyl-2-naphthylamine is evidently due to the intense light absorption at the surface layer of the vulcanizate by the phenyl-2-naphthylamine itself. Such behavior is typical also of other light-sensitizers[6]. Aldol-1-naphthylamine too behaves analogously to phenyl-2-naphthylamine in the polybutadiene vulcanizate (Figure 3).

(c). The introduction of light-filtering materials, in particular carbon black (3–5 per cent or more), sharply shifts the ratio between the light and heat action in the direction of the latter, and can directly suppress the sensitizing action of the heat-aging inhibitor, and thereby allow its inhibiting action to appear to the fullest. In this manner, a light-filter shields from light, not only the rubber part of the vulcanizate, but also the sensitizer.

Figure 4 shows that, in the presence of 3 or more parts of carbon black per 100 parts of the rubber, phenyl-2-naphthylamine acts only as a protector of the vulcanizate against light. The dye Sudan black (Table 1) likewise has an effect similar to that of carbon black.

If two heat-aging inhibitors sensitized a vulcanizate to light of different wavelengths, then it might happen that each would play the role of protective light-filter to the other; i.e., a mixture of two such sensitizers would protect the vulcanizate from the action of light. This, apparently, is what takes place when phenyl-2-naphthylamine and aldol-1-naphthylamine are used together (Table 1).

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KINETICS OF THE OXIDATION OF RUBBER UNDER THE INFLUENCE OF LIGHT *

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A number of investigators have established that the action of ultraviolet light on rubbers in the absence of oxygen causes considerable changes in their structure. For example, exposure of films of sodium-butadiene and natural rubbers results in a decrease of unsaturation and solubility, and by the evolution of gaseous products (hydrogen and methane)[1], and exposure of rubber solutions by a decrease of viscosity at first, followed by gel formation[2]. It has also been established that the simultaneous action of light and oxygen on rubbers causes even greater changes[3]. However, the studies of the light oxidation of rubbers are fundamentally qualitative. Systematic data on the kinetic laws of these processes are lacking.

The present study is devoted to the kinetics of the light oxidation of certain rubbers. Sodium-butadiene rubber was the principal object of study. Sheets of purified rubbers were photooxidized. The specimens were exposed to a mercury-quartz lamp PRK-2 at a distance of 25 cm. through a light-filter (pyrex glass), reflecting rays with $\lambda = 2960$ Å (these rays are not present in the sunlight which passes through the atmosphere). The kinetics of photooxidation were studied volumetrically in an apparatus described earlier[4].

The curves of photooxidation of various rubber structures at 60° are shown in Figure 1. It is seen from Figure 1 that the light oxidation of these rubbers proceeds at a constant rate. In this figure, the curves of light oxidation (*1–3*) and heat oxidation (*4–6*) of sodium-butadiene rubber at 40°, 60° and 70° are shown in Figure 2. In this temperature range, photooxidation maintains a linear character and ends in 12–14 hours. In this period, heat oxidation can not develop into an autocatalytic process. The decrease of unsaturation by 12 hours reaches 55 per cent in the case of photooxidation, and 6–8 per cent for heat oxidation.

Various experiments were set up to establish the influence of the diffusion of oxygen on the rate of oxidation of rubber.

As is shown in Figure 2, the kinetic curves of oxidation of rubber films 50, 100 and 200μ thick are superimposed.

The following experiments were also carried out. After the reaction ends at the point marked by an arrow in curve *1* in Figure 2, the oxidized films 50 and 100μ thick were ground to a powder and again subjected to photooxidation. No absorption of oxygen was observed. These experiments indicate the absence of any obstacles to diffusion during oxidation.

In order to establish the order of the oxygen reactions the kinetics of light oxidation was studied at oxygen pressures of 760 and 200 mm. mercury. It is seen from Figure 2 (curve *1*) that the rate of oxidation does not depend on the oxygen concentration, i.e., the reaction has a zero order.

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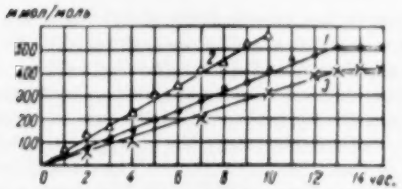

FIG. 1.—Relation between amount of oxygen absorbed by rubber and exposure time. Sheets were 100μ thick; oxygen pressure was 760 mm. mercury at 60° C. 1—Sodium-butadiene rubber. 2—Natural rubber. 3—Butyl rubber. The abscissa indicates the hours of exposure; the ordinate the millimoles per mole.

Experiments were carried out for the measurement of the light energy absorbed by the rubber during oxidation, and the quantum yield was calculated for the absorbed oxygen. The value of the quantum yield was 0.5 and remained constant throughout the period of exposure.

In order to explain the existence of a light after-effect, films 100μ thick were exposed for 6 hours at 40°, and then the reaction in darkness was investigated.

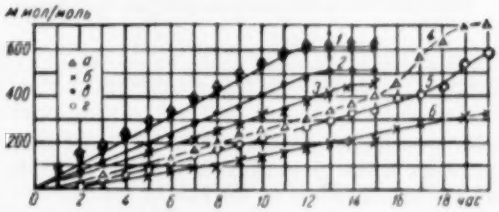

FIG. 2.—Relation between amount of oxygen absorbed by sodium-butadiene rubber and time. The abscissa indicates the hours of exposure; the ordinate the millimoles per mole.

1 △—Thickness 100μ, temperature 70°, oxygen pressure during exposure 760 mm. mercury
1 ×—Thickness 100μ, temperature 70°, oxygen pressure during exposure 200 mm. mercury
1 ●—Thickness 50μ, temperature 70°, oxygen pressure during exposure 760 mm. mercury
1 ○—Thickness 200μ, temperature 70°, oxygen pressure during exposure 760 mm. mercury
2 —Thickness 100μ, temperature 60°, oxygen pressure during exposure 760 mm. mercury
3 —Thickness 100μ, temperature 40°, oxygen pressure during exposure 760 mm. mercury
4 —Thickness 100μ, temperature 70°, oxygen pressure in darkness 760 mm. mercury
5 —Thickness 100μ, temperature 60°, oxygen pressure in darkness 760 mm. mercury
6 —Thickness 100μ, temperature 40°, oxygen pressure in darkness 760 mm. mercury

Oxidation was also carried out in darkness without previous exposure. The results are presented in Figures 3 (curves *1* and *2*). Figure 3 shows that the after-effect of light is negligible, that is, the rate of oxidation after the light is shut off (curve 2) is equal to the reaction in darkness (curve *1*).

It is necessary to observe that when rubber films are exposed to the entire emanation of a PRK-2 lamp, a considerable light after-effect is observed, as is shown in Figure 3 (curve *3*). This effect was observed in another study[5].

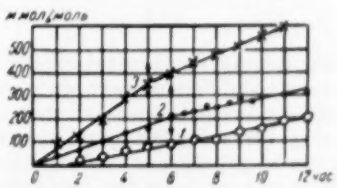

FIG. 3.—Photo-after-effect. Oxygen absorption at 40° C. 1—In darkness. 2—Interrupted exposure, $\lambda > 2960$ Å. 3—Interrupted exposure to entire radiation of PRK-2. The abscissa indicates the hours of exposure; the ordinate the millimoles per mole.

In order to compare the kinetic laws of light and heat oxidation, experiments were carried out at the same temperatures (40°, 60°, and 70°) in darkness. The results are shown in Figure 2 (curves *4–6*).

One of the authors demonstrated[6] that, in the heat oxidation of rubbers in the temperature range 80–130°, the rate of the process depends directly on the concentration of stable peroxides, since the energy of the reactions is exhausted, largely on account of their decomposition. The data obtained by the authors for heat oxidation at lower temperatures (40–70°) agree with the laws observed at higher temperatures.

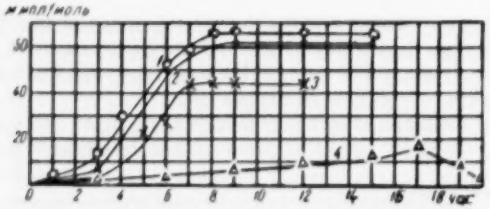

FIG. 4.—Relation between amount of peroxide compounds formed during oxidation of sodium-butadiene rubber and time. Thickness of sheets 100μ, oxygen pressure 700 mm. mercury. 1—During exposure at 70°; 2—During exposure at 60°; 3—During exposure at 40°; 4—In darkness at 70°. The abscissa indicates the hours of exposure; the ordinate the millimoles per mole.

It is seen from a comparison of curves *1–3* of Figure 2 and curves *1–3* of Figure 4 that a change in the concentration of stable peroxides during photooxidation has no appreciable effect on the rate of the reaction, which remains constant throughout the experiment.

It was shown in a special series of experiments that the peroxides formed during photooxidation of rubber are stable (at 40–70°) and do not decompose under the action of light in a high vacuum.

TABLE 1

AMOUNT OF OXYGEN IN ACIDS AND COMPOUND ESTERS IN OXIDIZED RUBBER

Exposure time (hrs.)	60° C			70° C		
	Oxygen in acids and esters (mmole/mole)	Oxygen absorption (mmole/mole)	Oxygen in acids and esters (% of absorbed O_2)	Oxygen in acids and esters (mmole/mole)	Oxygen absorption (mmole/mole)	Oxygen in acids and esters (% of absorbed O_2)
3	16	122	13.1	19	136	14.0
6	31	221	14.0	37	300	12.3
9	45	350	12.8	55	465	11.8
12	61	470	13.0	73	615	11.9
15	72	510	14.2	94	615	15.3

Consequently, photooxidation develops principally at the expense of photoinitiation, and this is a radical difference between it and heat oxidation.

Since one of the authors[6] already established that, in the majority of actual cases, heat oxidation of rubbers is limited by the acts of initiation, it was interesting to compare the rate of initiation of heat and light oxidation. A calculation made at 70° showed that while for the photo-process $W_C = 2.92 \times 10^{-4}$ ml./sec. for the thermal process $W_T = 1.5 \times 10^{-9}$ ml./sec., that is, the rate of photo-initiation is 5 orders greater than that of heat-initiation. Thus, photo-

initiation is very intensive. This difference of the rates of the light and heat processes is due to the great difference in the activation energies of light (E_C = 5–6 kcal./mole) and heat (E_T = 21–22 kcal./mole) oxidation.

Analysis of the solid phase of oxidized rubber showed that 10–15 per cent of the bound rubber is necessary for the acid and complex ester fraction (see Table 1).

TABLE 2

KINETICS OF ACCUMULATION OF VOLATILE BY-PRODUCTS (HCOOH)

Oxidation temperature (° C)	Oxidation time (hours)	Weight of unoxidized sheet (g.)	Oxygen absorption (g.)	Oxygen in volatiles (g.)	Oxygen in volatiles (% of absorbed O_2)
40	3	0.2245	0.012	0.0048	40.00
40	6	0.2310	0.026	0.0104	40.00
40	9	0.2305	0.036	0.0144	40.00
60	3	0.2304	0.013	0.0052	40.00
60	6	0.2302	0.030	0.0120	40.00
60	9	0.2350	0.041	0.0165	40.20
70	3	0.2318	0.015	0.0063	42.00
70	6	0.2210	0.034	0.0137	40.30
70	9	0.2205	0.052	0.0209	40.20

Forty per cent of the oxygen appeared as volatile byproducts, consisting essentially of formic acid. The data are presented in Table 2. Twenty per cent of the oxygen was in the form of peroxides. No carbonyl groups or water were detected in the reaction products.

Thus, about 70–75 per cent of the total bound oxygen was present in the form of various functional groups.

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THE DIFFUSION AND SOLUBILITY OF OXYGEN AND HYDROGEN IN SODIUM-BUTADIENE RUBBER AT VARIOUS STAGES OF ITS OXIDATION *

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We have studied the diffusion and solubility of oxygen and hydrogen in thin strips (about 50μ and thinner) of sodium-butadiene (polybutadiene) rubber at temperatures of 40°, 60°, 80°, and 100° C. The experiments were carried out, not only on the unoxidized rubber, but also on strips which had previously been oxidized to stages of oxidation corresponding to an absorption of 50, 150, 250, 350, and 450 millimoles of O_2 by 54 grams (one mole) of the polymer[1].

In cases where the thickness of strips amounted to about 1 mm., all the authors who have studied the diffusion of gases in elastomers[2] have declared Fick's law to be correct:

$$\frac{dQ}{dt} = \frac{S \cdot D(c_1 - c_2)}{l} = \frac{S \cdot D \cdot \sigma(p_1 - p_2)}{l} \tag{1}$$

where Q is the quantity of the diffusing gas; S is the area of the strip; D is the coefficient of diffusion; c_1 and c_2 are the equilibrium concentrations of dissolved gas at both its surfaces, the gas pressures on both sides being p_1 and p_2, respectively; σ is the solubility coefficient of the gas in the rubber; l is the thickness of the strip; and t is time.

In experiments with thin strips of rubber, and especially strips of oxidized rubber, we noticed pronounced deviations from Fick's law[3]. These deviations are evidently kinetic in nature, and are connected with certain boundary resistances at the rubber-gas surface of separation. For this case, Equation (1) is converted to:

$$\frac{dQ}{dt} = \frac{SD(c_1 - c_2)}{l}\left(1 - \frac{2D}{kl + 2D}\right) = \frac{SD\sigma(p_1 - p_2)}{l}\left(1 - \frac{2D}{kl + 2D}\right) \tag{2}$$

where k is the "gaseous penetration of the boundary layer"—a quantity which is the reciprocal of the boundary resistance. The value k may be found by a comparison of the rates of the steady flow of the diffusing gas for several different thicknesses of strips (all at just the same stage of rubber oxidation). The accuracy of such a determination of k is not very great. Still, it may be considered an established fact that the amount of the gaseous penetration of the boundary layer decreases with an increase of the degree of oxidation of the rubber, and increases with a rise of temperature. Table 1 presents the values that we obtained for k.

For the measurement of the coefficients of diffusion D and of solubility σ of hydrogen and oxygen, we employed the following method, evolved by Daynes[4].

* Translated for Rubber Chemistry and Technology by Malcolm Anderson from *Doklady Akademii Nauk SSSR*, Vol. 99, No. 6, pages 1053–1056 (1954).

TABLE 1

COEFFICIENT OF GASEOUS PENETRATION OF THE BOUNDARY LAYER, FOR H_2 AND O_2 AT VARIOUS STAGES OF THE RUBBER OXIDATION

Degree of oxidation (millimoles O_2/mole)	Temperature (° C)	Gas penetration of the boundary layer (cm./sec.)	
		H_2	O_2
0	60–100	>3*	>3
50	60	0.2	0.008
50	100	0.53	0.049
150	80	0.16	—
150	100	0.24	—
350	100	0.15	—

* When $k > 3$, the quantity $2D/(kl + 2D)$ in Equation (2) approaches our experimental error in the determination of the rate of flow of the diffusing gas, and hence it is impossible to determine k.

A gas is admitted into both parts of a diffusion chamber divided into halves by the strip which is being tested, the gas being under pressures of p_1 and p_2, respectively, in the two parts. Now after a constant rate is achieved, the total amount of gas which has been diffused from the beginning of the test equals the constant rate of diffusion[5] (given by the slope of the straight portion of the curve of $Q = f(t)$), multiplied by the time t from the start of the experiment minus some amount of time lag τ:

$$Q_t = \left(\frac{dQ}{dt}\right)_{\text{const.}} (t - \tau) \tag{3}$$

The time lag τ (where $kl \gg 2D$) is related to the diffusion coefficient by the ratio[5]:

$$\tau = \frac{l^2}{6D} \frac{c_1 + 2c_2 - 3c_0}{c_1 - c_2} \tag{4}$$

where c_0 is the initial uniform concentration of gas in the strip. When kl is commensurate with D, Equation (4) is inapplicable. However for this case, we have found, there is a numerical relation between τ and D. It is given by the equation

$$\tau = \frac{2l^2}{D(c_1 - c_2)} (1 + 2\alpha)[A_1 c_1 + A_2 c_2 - (A_1 + A_2)c_0] \tag{5}$$

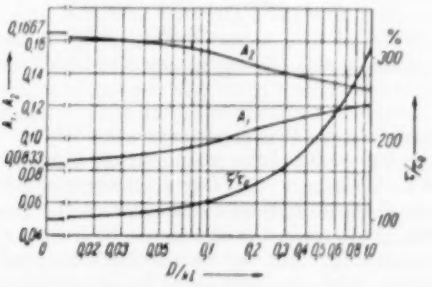

FIG. 1.

where

$$A_1 = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{\beta_n^2(1 + \alpha^2\beta_n^2 + 2\alpha)}, \quad A_2 = \sum_{n=1}^{\infty} \frac{1}{\beta_n^2(1 + \alpha^2\beta_n^2 + 2\alpha)}$$

Here $\alpha = D/kl$, β_n is the nt^h root of the equation $2 \cot \beta = \alpha\beta - \frac{1}{\alpha\beta}$.

The relation (5) makes it possible, by the use of the method of successive approximations, to calculate D from the value of τ also in those cases where, as

TABLE 2

COEFFICIENTS OF DIFFUSION AND SOLUBILITY * AND THE ACTIVATION ENERGY OF THE DIFFUSION OF HYDROGEN AND OXYGEN IN A SODIUM-BUTADIENE RUBBER

Degree of oxidation in millimoles of absorbed O_2 by 1 mole of polymer	Temp. °C	System: rubber-hydrogen			System: rubber-oxygen		
		$D \times 10^6$ cm.²/sec.	E_1 cal./mole	$\sigma \times 10^6$ cc./cc. × mm. Hg	$D \times 10^6$ cm.²/sec.	E_1 cal./mole	$\sigma \times 10^6$ cc./cc. × mm. Hg
0	40	0.42	8100	0.35	0.092	9800	1.23
0	60	0.92		0.37	0.24		1.28
0	80	1.87		0.37	0.57		1.23
0	100	3.28		0.41	1.19		1.27
50	40	0.56	7900	0.35	0.118	9700	1.19
50	60	1.22		0.36	0.31		1.26
50	80	2.34		0.38	0.695		1.36
50	100	4.11		0.40	1.42		1.41
150	40	0.26	8600	0.37	0.021	10800	1.11
150	60	0.65		0.34	0.058		1.17
150	80	1.34		0.34	0.145		1.23
150	100	2.73		0.33	0.324		1.31
250	40	0.085	9100	0.45	0.0061	11600	1.12
250	60	0.22		0.43	0.0185		1.19
250	80	0.50		0.43	0.053		1.09
250	100	0.94		0.43	0.125		1.18
350	40	0.072	9300	0.33	0.0048	11900	0.90
350	60	0.18		0.34	0.016		0.93
350	80	0.43		0.32	0.044		0.82
350	100	0.78		0.36	0.106		0.96
450	40	0.057	9600	0.31	0.0044	12100	0.71
450	60	0.15		0.34	0.014		0.74
450	80	0.31		0.30	0.040		0.70
450	100	0.73		0.28	0.096		0.76

* The coefficient of solubility is determined from the ratio in Equation (2), for the linear portion of the curve of $Q = f(t)$.

in a set of our experiments, D is commensurate with kl. Figure 1 gives the values of A_1 and A_2 for values of the parameter D/kl from 0 to 1, as well as the change in τ when D/kl changes from 0 to 1 for the case where $c_2/c_1 = 0.8$ and $c_0 = 0$. As we see, if we do not take into account the gaseous penetration of the boundary layer, the error in the calculation of D from τ (for large values of D/kl) can be considerable. For the values of k presented in Table 1 for the system oxygen-rubber, this error, in strips of the same thickness as ours, amounts to 10–15 per cent.

The dependence of the diffusion coefficient on temperature in the range 40–100° C is given by the expression

$$D = D_0 e^{-E_1/RT} \tag{6}$$

The values we obtained for the coefficients of diffusion and solubility are shown in Table 2. The values for E_1, the activation energy for the diffusion of the respective gases, are also shown there.

It is interesting to compare the values obtained for sodium-butadiene rubber, at various stages of its oxidation, with the values derived by Barrer for natural rubber at various stages of vulcanization; i.e., for vulcanizates with different sulfur contents.

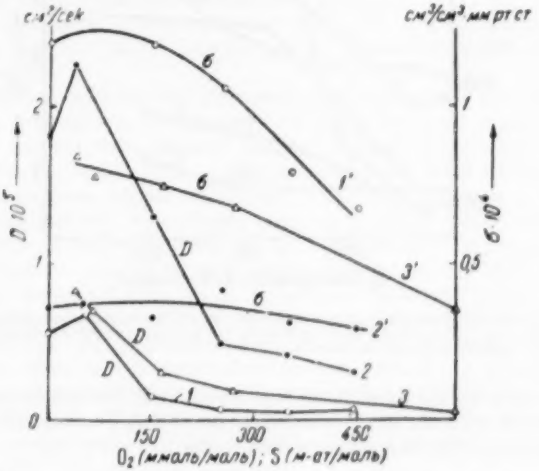

FIG. 2.—The abscissa represents oxygen absorption in millimoles/mole and sulfur consumption in g.-atoms × 1000/mole. The ordinate at left represents $D \times 10^5$ in sq. cm. per second; that at right, $\sigma \times 10^4$ in cc./(cc. × pressure in mm. mercury).

Figure 2 gives a graphic presentation of the change of the diffusion coefficient D of hydrogen (curve *2*) and oxygen (*1*) in sodium-butadiene rubber at various stages of its oxidation (our data) and the diffusion coefficients of nitrogen (*3*) in vulcanizates of natural rubber differing in their sulfur content (temperature, 80° C)[6]. It can be seen that as the oxygen content increases, the diffusion coefficients of oxygen and hydrogen decrease (not counting the small increase when unoxidized rubber becomes oxidized to the extent of 50 millimoles O_2/mole) in a way fully analogous to the way in which the diffusion coefficient in natural rubber decreases when the sulfur content increases.

The solubility of hydrogen (Figure 2, curve *2'*) in sodium-butadiene rubber during oxidation changes hardly at all, while the solubility of oxygen (Figure 2, *1'*) changes but slightly, which is similar to Barrer's findings for nitrogen solubility (Figure 2, *3'*) in natural rubber vulcanizates with various sulfur contents. The change of the activation energy E_1 of diffusion during the oxidation of rubber (see Figure 3, curve *1*—oxygen, curve *2*—hydrogen) or the increase of the sulfur content of the vulcanizate (Figure 3, curve *3*), as well as the increase of the degree of oxidation of sodium-butadiene rubber (our data:

curve 1′—oxygen, curve 2′—hydrogen) and with an increase of the sulfur content of a natural rubber vulcanizate[7] all proceed in exactly the same direction. Thus in spite of the great differences in character between the reaction products of the oxygen and sulfur combination reactions, both these reactions change the diffusion properties in the system : rubber-gas, in quite similar ways. Evidently

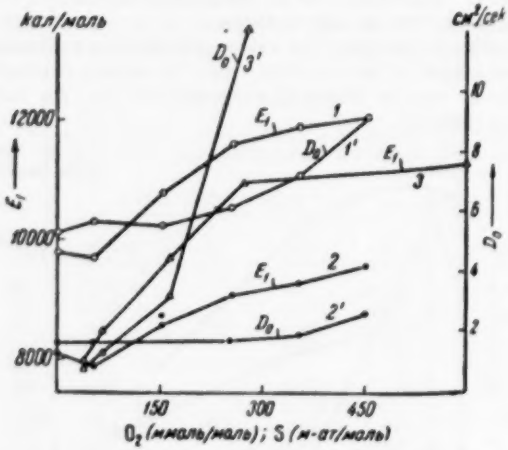

FIG. 3.—The abscissa represents oxygen absorption in millimoles/mole and sulfur consumption in g.-atoms × 1000/mole. The ordinate at left represents the activation energy for diffusion, E_1, in calories per mole; that at right D_0 in sq. cm. per second.

the difference in the nature of the groups which "tie" the rubber chains together in the course of vulcanization or oxidation, plays only a minor role in the change in diffusion properties as a result of such tying.

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[5] The change in the pressures p_1 and p_2 on both sides of the strip in our experiments amounted to less than 1 per cent of the drop in pressure $p_1 - p_2$, and therefore this change may be disregarded.
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STUDY OF THE THERMAL OXIDATION OF BUTADIENE-NITRILE ELASTOMERS*

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A large number of rubber products used at high temperatures are manufactured from vulcanized butadiene-nitrile elastomers. Although great attention has been devoted in recent years to the question of the oxidation of natural rubber[1], there has been no special study of the thermal oxidation of butadiene-nitrile elastomers.

Both butadiene-acrylonitrile elastomers themselves and their vulcanizates show various peculiarities of behavior. It is known that, in the presence of acrylonitrile, the polymerization of butadiene takes place principally in the direction of the formation of 1,4-polymers. It is also known that, in natural rubber, polybutadiene, butadiene-styrene copolymers, and other elastomers[1], the double bonds of the main chains react most readily with oxygen. One would, therefore, expect to find an analogy between the behavior on oxidation of butadiene-nitrile copolymers and natural rubber, which also has a linear structure and contains double bonds in the main molecular chains.

However, the properties of nitrile rubbers are quite unlike those of natural rubber, e.g., vulcanized nitrile rubbers are characterized by their very high heat resistance, and their aging is marked by the predominance of structure formation, whereas vulcanized natural rubber is destroyed during aging.

Nitrile rubbers are difficult to plasticize by ordinary methods, and plasticization is possible only by the addition of special substances which activate oxidation processes.

The behavior of butadiene-nitrile rubber and its vulcanizates cannot be explained on the basis of laws which apply to the oxidation of natural rubber, polybutadiene, butadiene-styrene copolymers, etc. This was the reason for undertaking the present study.

Different types of butadiene-nitrile rubbers produced industrially were studied, namely: SKN-18, SKN-26, and SKN-40, which contain varying proportions of acrylonitrile.

Inhibited oxidation of the rubbers was the principal subject of the study. This was prompted by the fact that substances such as sulfur, vulcanization accelerators, and age resistors, which retard oxidation are always present normally in vulcanized rubber. Consequently, the behavior of a vulcanizate in service always depends on the course of inhibited oxidation.

The study of the kinetics of oxidation of butadiene-nitrile rubbers, both alone and in the presence of the most widely used oxidation inhibitor, phenyl-2-naphthylamine, showed that there is a definite relation between the rate of oxidation of such rubbers and their acrylonitrile contents. In the case of free oxidation, this relation is observed only at low temperatures (100° and lower) (Figure 1). In the presence of phenyl-2-naphthylamine, the rate of oxidation

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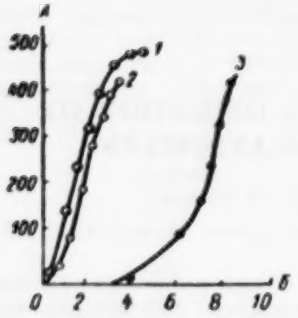

FIG. 1.—Kinetics of combination of oxygen in the oxidation of rubbers. Temperature 100° C. A—Quantity of O_2 in millimoles per double bond. B—Time in hours. 1—SKN-26, 2—SKN-18, 3—SKN-40.

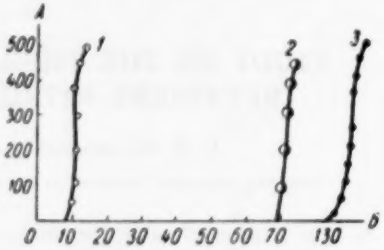

FIG. 2.—Kinetics of combination of oxygen in the oxidation of rubbers containing 12 millimoles per l. of phenyl-2-naphthylamine. Temperature 100° C. A—Quantity of O_2 in millimoles per double bond. B—Time in hours. 1—SKN-18, 2—SKN-26, 3—SKN-40.

throughout the temperature range studied (Figure 2) becomes greatly retarded with increase of the acrylontrile content.

These experiments establish the fact that the oxidation of nitrile rubbers is characterized by the elimination of substances which are volatile under the experimental conditions. Thus, for example, at 120°, the amount of volatile substances comprises about 7 per cent of the weight of the rubber. At the same time it was observed that a certain quantity of byproducts soluble in alcohol is formed during oxidation (unoxidized butadiene-nitrile rubbers are insoluble in alcohol) (Figure 3). Such results indicate that decomposition of the rubber molecules takes place during oxidation.

Structural changes in nitrile rubbers and their vulcanizates during oxidation were studied on the basis of the changes in their solubility in chloroform and in their mechanical properties (equilibrium moduli and rate of relaxation).

The results of these experiments are shown in Figures 4, 5, and 6. As is seen in these figures, the rate of change of these factors varies with SKN-18, SKN-26, and SKN-40 rubbers. While the changes of solubility, equilibrium modulus, and relaxation constant[2] of vulcanizates of SKN-18 are continuous during aging (as in the case of oxidation of polybutadiene), in SKN-26 and

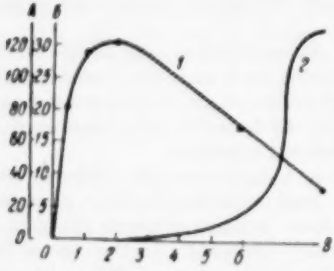

FIG. 3.—Kinetics of accumulation of byproducts soluble in alcohol during oxidation of SKN-40. Temperature 100° C.

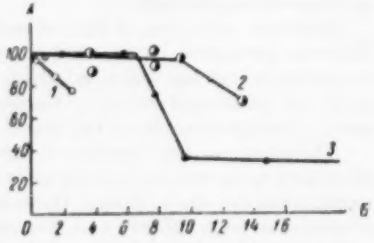

FIG. 4.—Change of solubility of rubber in chloroform in oxidation at 120° C. A—Amount of dissolved fraction in percentage. B—Aging time in hours. 1—SKN-18, 2—SKN-26, 3—SKN-40.

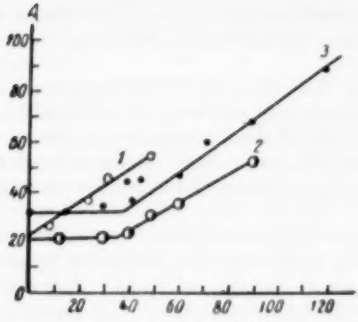

FIG. 5.—Change of equilibrium modulus of heat vulcanizates during aging. Temperature 120° C. A—E_∞ in kg. per sq. cm. B—Aging time in hours. 1—Vulcanized SKN-18. 2—Vulcanized SKN-26. 3—Vulcanized SKN-40.

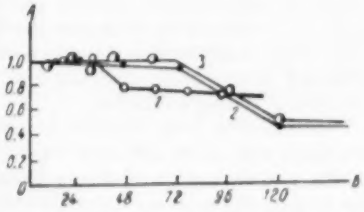

FIG. 6.—Change of relaxation constant of heat-vulcanizates during aging. Temperature 120° C. A—Change of relaxation constant. B—Aging time in hours. 1—Vulcanized SKN-18. 2—Vulcanized SKN-26. 3—Vulcanized SKN-40.

SKN-40, a long oxidation period is observed, during which practically no change of the properties of either the raw rubbers or their vulcanizates takes place.

Investigation of the kinetics of consumption of phenyl-2-naphthylamine (Figure 7) showed at least two peculiarities in this process during the oxidation of butadiene-nitrile rubbers at 110–130° which are not observed in the oxidation of other types of rubber.

(1) The rate of consumption of phenyl-2-naphthylamine during oxidation of all the butadiene-nitrile rubbers studied does not continue at a constant value, whereas the rate of consumption of phenyl-2-naphthylamine during oxidation of polybutadiene, butadiene-styrene copolymers, and natural rubber is constant; practically no consumption of phenyl-2-naphthylamine is observed for a long period after the beginning of oxidation of SKN-26 and SKN-40 rubbers.

(2) Autocatalytic oxidation commences in the presence of a small quantity of unbound phenyl-2-naphthylamine.

These peculiarities in the behavior of SKN-26 and SKN-40, i.e., the peculiar kinetics of consumption of phenyl-2-naphthylamine and retention of the original

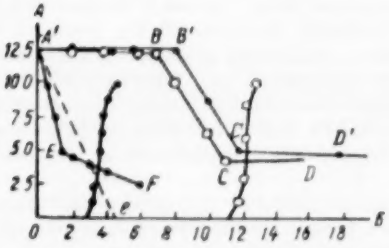

FIG. 7.—Kinetics of consumption of phenyl-2-naphthylamine in the oxidation of rubber. Temperature 120° C. A—Phenyl-2-naphthylamine in millimoles per l. of rubber. B—Time in hours. ABCD—SKN-26. A'B'C'D'—SKN-40. A'EF—SKN-18. A'b—Polybutadiene.

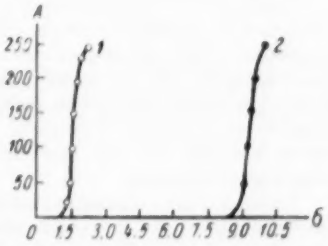

FIG. 8.—Influence of byproducts of oxidation of SKN-40 extracted with alcohol on the kinetics of oxidation of polybutadiene. Oxidation temperature 120° C. A—Amount of O_2 absorbed in cc. per g. of rubber. B—Time in hours. 1—Polybutadiene. 2—Polybutadiene containing products of oxidation of SKN-40.

properties of the unvulcanized and vulcanized rubbers in the initial stages of oxidation, are connected with the formation of substances which can inhibit the oxidation of these rubber (Figure 8).

The property of inhibiting oxidation is characteristic of the byproducts of oxidation only of nitrile rubbers, and is not observed with other types of rubber; hence it is reasonable to ascribe the formation of these substances to the presence of acrylonitrile chains in the molecules of these rubbers. Some of the data obtained in this study indicate that the nitrile groups of the rubber undergo conversion during oxidation.

Nitriles are very reactive compounds. Their reduction, saponification, reactions with aldehydes and organic acids, polymerization, oxidation by peroxides, and absorption of other substances are well known reactions. Peroxides, aldehydes, and acids are formed during the oxidation of rubber. Consequently, a reaction between these substances with the nitrile groups of the rubber molecules is possible.

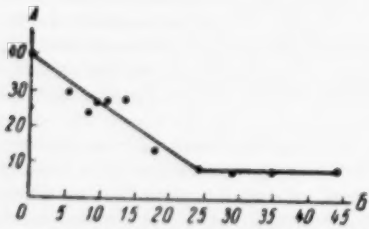

FIG. 9.—Kinetics of consumption of phenyl-2-naphthylamine in the oxidation of saponified SKN-26. Temperature 120° C. A—Consumption of phenyl-2-naphthylamine in millimoles per l. of rubber. B—Time in hours.

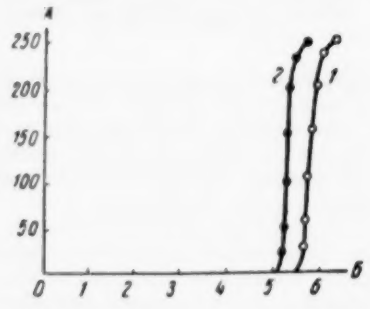

FIG. 10.—Kinetics of combination of oxygen in the oxidation of polybutadiene in the presence of polyacrylonitrile. Temperature 100° C. A—Amount of O_2 absorbed in cc. per g. of rubber. B—Time in hours. 1—Polybutadiene. 2—Mixture of polybutadiene and polyacrylonitrile.

The conversions which the acrylonitrile chains of the rubber molecules undergo during oxidation lead to the formation of a large quantity of various substances.

A study of the conditions of formation and the properties of the products of oxidation of butadiene-nitrile rubbers showed that not all the products of oxidation soluble in oxygen are capable of inhibiting oxidation. These substances are formed during the oxidation, and heating the rubber in nitrogen for a long time does not lead to the formation of inhibitors of oxidation. Decomposition accompanies formation of inhibitors during oxidation of butadiene-nitrile rubbers, and the most rapid decomposition is observed in the initial stages of the process.

Autoinhibition during oxidation of nitrile rubbers is the cause of their great heat resistance, and it explains the characteristic peculiarities of their oxidation and the changes in their mechanical properties during this process.

For example, the lack of consumption of phenyl-2-naphthylamine in the early stages of oxidation indicates that inhibition here is due to the products of oxidation of the rubber itself. In fact, during the oxidation of a saponified SKN-26 rubber (which no longer contains nitrile groups), the kinetics of con-

sumption of phenyl-2-naphthylamine, as is shown in Figure 9, do not differ from the kinetics of consumption during the oxidation of other butadiene rubbers.

In a separate series of experiments, a mixture of polybutadiene and polyacrylonitrile was oxidized; in this mixture the ratio of the butadiene to nitrile units was the same as in SKN-26 (Figure 10). During oxidation of this mixture, no autoinhibition effect was observed, and no inhibitors were formed. Furthermore, acrylonitrile is not even involved in a conjugate oxidation process with polybutadiene. Consequently, the peculiar behavior of nitrile rubbers is due, not only to the presence in the system of butadiene and nitrile chains, but also to their distribution in the molecules of the polymer.

CONCLUSIONS

1. Processes of destruction and structure formation take place during the thermal oxidation of butadiene-nitrile rubbers. These processes take place simultaneously, and are the result of absorption of oxygen by the rubber molecules. The dominant process, which governs the changes in the physical and mechanical properties of rubber, is structure formation.

2. An essential difference between the behavior of vulcanizates of SKN-18 on the one hand, and of SKN-26 and SKN-40 on the other, is shown by heat oxidation and aging. Depending on the length of the induction period of oxidation inhibited by phenyl-2-naphthylamine, the nature of the consumption of inhibitor, and the rate of change of the equilibrium modulus, relaxation constant, and standard physical-mechanical properties during aging, the behavior of SKN-18 is practically the same as that of other butadiene polymers containing an equal number of double bonds in the main chains of the molecules.

3. It was established that, during thermal oxidation of butadiene-nitrile copolymers, acrylonitrile chains of the rubber molecules undergo conversion.

4. The formation of a certain quantity of substances soluble in methyl and ethyl alcohol during oxidation of nitrile rubbers is revealed, and it is established that substances present in these byproducts can inhibit the oxidation of rubber.

5. The resistance of butadiene-nitrile rubbers to thermal inhibited oxidation and aging of vulcanizates, which is greater than that of other butadiene rubbers, is explained by the formation from the rubber itself, during oxidation, of substances which are, in combination with phenyl-2-naphthylamine, very strong inhibitors of the oxidation process.

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[2] The relaxation constant in this study is a characteristic of the rate of the relaxation processes in a deformed specimen after the load is removed, and is equal to the product of the rate of restoration and the time of restoration.

DETERMINATION OF SULFUR IN RUBBER VULCANIZATES *

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The determination of organically bound sulfur in rubber compounds presents a problem to the analytical chemist. A rubber vulcanizate may contain sulfur that is present in the free state, sulfur that is combined with the rubber or in other organic compounds, and sulfur in inorganic compounds.

The free sulfur can be determined after its removal by extraction. The sulfur that is combined with the rubber and other organic material and the sulfur contained in the inorganic fillers are usually determined together. A separate determination of the sulfur present in the inorganic fillers is then made in order to calculate the amount of sulfur that is organically combined.

Combustion methods are often used to determine sulfur, and the rapidity and accuracy of such methods make them suitable for many types of analyses. At temperatures of 1350° C and higher, the total sulfur in rubber vulcanizates can be determined[1].

The rubber technologist, however, is usually more interested in organic sulfur than in total sulfur. Accordingly, an investigation of the combustion method at lower temperatures was undertaken. The compounds used in this study were also analyzed by the fusion and by the zinc-nitric acid methods for comparative purposes.

EXPERIMENTAL

A combustion method for the determination of sulfur in rubber may be divided into three phases: decomposing the specimen, collecting the evolved gases, and determining the amount of sulfur evolved.

Decomposing the specimen.—A rubber hydrocarbon can be distilled from a rubber compound below red heat. Wall[2], in work on the thermal decomposition of rubbers for mass spectrometric investigations, used a temperature of 400° C in a high vacuum, because lower temperatures did not completely decompose the polymers. In analysis of GR-S carbon black masterbatches[3], 550° C is used to remove the polymer in determining the ash and the carbon black. At 550° C, any lithopone used in rubber compounds decomposes slightly with evolution of hydrogen sulfide, which leads to high results for sulfur; at temperatures of 400° C pyrolysis of the rubber always may not be completed during the time allowed. Therefore, a temperature of 480° C to 500° C appears to be optimum for the purpose of this investigation. The combustion of the rubber sample was accomplished by using the two-unit electric organic combustion furnace shown in Figure 1. The 8-inch unit was placed at the exit end of the combustion tube, and was maintained at a temperature of 850° to 900° C. The 12-inch unit which was placed next to the smaller unit was maintained at a temperature of 480° to 500° C. The upper part of each unit was hinged to

* Reprinted from *Analytical Chemistry*, Vol. 27, No. 10, pages 1606–1609, October 1955. The present address of E. W. Zimmerman is the Aluminum Match Plate Corporation, Buffalo, N. Y.

facilitate installing the combustion tube and the thermocouples. An unglazed porcelain McDanel combustion tube, 30 inches long, 1¼-inch outside diameter, 1-inch inside diameter, with a standard tapered tip and equipped with a sample inserter was found to be very satisfactory.

To obtain a clean decomposition, it was necessary to adjust the specimen size to a minimum compatible with the precision desired, to control the rate of decomposition of the specimen to avoid minor explosions, and to use sufficient oxygen to burn completely the volatilized organic material to avoid having soot enter the absorber. The specimens contained approximately 0.15 gram of hydrocarbon; and since the compounds contained about 65 per cent hydrocarbon by weight, 0.25-gram specimens were used throughout this work.

A specimen of ground rubber vulcanizate was accurately weighed, transferred to a 10 × 75 mm. test-tube, and tapped into the bottom with a glass rod. The test-tube was laid in a porcelain combustion boat, which was placed in the cool portion of the combustion tube with the open end of the test-tube facing the outlet end of the combustion tube. The sample injector was inserted into the large end of the combustion tube, the oxygen flow was adjusted to 1100 cc. per minute, and the combustion boat was pushed into the center of the 12-inch

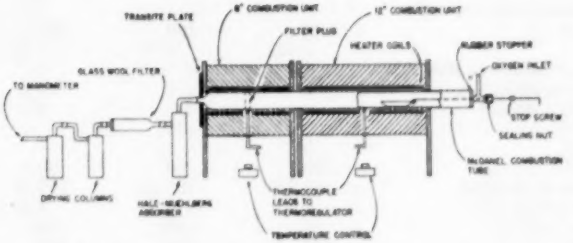

FIG. 1.—Assembly of apparatus for combustion method.

unit, which was maintained at about 500° C. The dense vapors that accompanied the intial decomposition of the specimen displaced the oxygen around the specimen and burned at the mouth of the test-tube. Thus, the rubber was permitted to decompose in an oxygen-poor atmosphere without a localized temperature rise.

Collecting the evolved gases.—Since the distillation of the rubber hydrocarbon occurred at a relatively low temperature, the gases were passed through a high-temperature zone to ensure complete combustion. This was accomplished with the 8-inch furnace unit maintained at about 900° C. A close-fitting porous ceramic plug may be used in the high temperature zone to filter the gas or to present more surface to facilitate oxidation, but is not essential.

Since sulfur trioxide was present in the evolved gases, the exit end of the combustion tube was maintained at a temperature of at least 200° C as suggested by Hale and Muehlberg[4]. This was accomplished by placing the tube so that the outlet tip was about 2 inches from the edge of the hot zone. A Transite baffle with a hole just large enough to admit the thick portion of the tip was mounted on the end of the furnace to reduce the heat loss in the furnace and protect the operator from the heat while manipulating the absorber.

A Hale-Muehlberg absorber, lubricated with heavy silicone grease, was connected to the McDanel combustion tube by means of a standard taper joint.

The absorber was charged with a solution prepared just prior to use by mixing 4 ml. of 5 per cent hydrogen peroxide solution, 18 ml. of 10 per cent sodium chloride solution (to prevent foaming during combustion), and 18 ml. of distilled water. The 5 per cent hydrogen peroxide solution was prepared by diluting 30 per cent ACS grade hydrogen peroxide that did not contain a stabilizer. This type of absorber, or even a battery of them, did not collect completely the sulfur trioxide, which was seen passing through in the form of a fog. This loss amounted to about 4 per cent of the evolved sulfur. However, when a glass tube containing a filter of dry glass wool was attached to the outlet end of the tower, this vapor was quantitatively collected. Approximately 10 grams of ordinary glass wool, previously leached in a warm 0.5 per cent hydrochloric acid solution and washed with distilled water until the washings were neutral to methyl red, was used to pack the filter tube. The exit end of the filter tube was fitted with a rubber stopper containing a short length of glass tubing to provide a connection to the drying columns and flow meter.

TABLE I

COMPOSITION OF COMPOUNDS

Batch designation	1	2	3	4
Original mixes, parts by weight				
Pale crepe	100	100	100	100
Sulfur	0.625	4.13	7.17	10.5
Tetramethylthiuram disulfide	0.3	—	—	—
Phenyl-2-naphthylamine	1	1	1	1
Diphenylguanidine	—	—	1	—
Lead oxide	—	10	—	—
Zinc oxide	5	—	—	—
Fillers added[a]	50	50	50	50
Total (parts by weight)	156.925	165.13	159.17	161.5
Free sulfur added (%)	0.50[b]	2.50	4.50	6.50
Cure: Time (min.)	30	30	30	60
Temp. (° C)	140	150	150	160

[a] Filler identity

	Compound designation			
Carbon black	1*A*	2*A*	3*A*	4*A*
Calcium carbonate	1*B*	2*B*	3*B*	4*B*
Barium carbonate	1*C*	2*C*	3*C*	4*C*
Lithopone	1*D*	2*D*	3*D*	4*D*

[b] Includes 0.16 gram of sulfur from organic accelerator.

Determining the amount of sulfur evolved.—After 10 minutes the oxygen flow was shut off, the boat was removed from the combustion tube, and the two absorbers were disconnected. The solution used to absorbe the gases was quantitatively removed from the tower and glass tubing, and particular attention was paid to thorough rinsing of the fritted disk and the inside surface of the connecting tubes. The glass wool filter was rinsed by mounting the glass tube on a small suction flask and washing it with 125 ml. of distilled water while using gentle suction. This was combined with the solution already collected in a 400 ml. beaker, four drops of methyl red indicator were added, and the solution was titrated with standardized 0.02*N* sodium hydroxide. The filter tube was prepared for the next run by rinsing with acetone and drying with compressed air.

RUBBER COMPOUNDS

Four rubber batches were carefully prepared on a parts per weight basis to represent the various types of mixes and concentrations of sulfur indicated in

Table I. Each of these batches was divided into four groups, and to each group was added one of the four selected fillers. The fillers included carbon black (Thermax), calcium carbonate (Whiting), barium carbonate, and lithopone.

The 16 rubber compounds, whose designations are listed in Table I, were analyzed for sulfur by the fusion method and the zinc-nitric acid method described in ASTM Standards on Rubber Products[5] and the Federal Test Method Standard[6]. They were also analyzed by the combustion method described herein. The residues remaining after the combustion of the compounds in

TABLE II

SULFUR DETERMINED BY COMBUSTION METHOD

Compound	No. of detn.	% Sulfur (av.)	Standard deviation
1*A*	4	0.39	0.033
2*A*	4	1.67	0.037
3*A*	5	4.49	0.078
4*A*	3	6.35	0.036
1*B*	4	0.30	0.031
2*B*	4	1.52	0.029
3*B*	5	4.32	0.062
4*B*	4	6.19	0.146
1*C*	5	0.27	0.038
2*C*	7	1.45	0.052
3*C*	7	4.13	0.047
4*C*	2	5.77	0.021
1*D*	11	0.56	0.125
2*D*	22	1.99	0.089
3*D*	8	4.54	0.085
4*D*	6	6.39	0.139

groups *A*, *B*, and *D* were analyzed for sulfur by oxidation with a bromine-nitric acid solution and precipitation as barium sulfate. Those of group *C* were analyzed by the fusion method since the wet oxidation procedure is inoperative in the presence of barium carbonate.

RESULTS BY COMBUSTION METHOD

Table II gives the average values for the sulfur evolved during combustion from each of the 16 compounds and also the standard deviations for the individual determinations. An analysis of these standard deviations indicates the existence of two levels of precision. Determinations made on samples of groups *A*, *B*, and *C*, which when compounded contained no inorganic sulfur, gave a standard deviation of the order of 0.04 per cent sulfur. Determinations made on samples of group *D*, which contained lithopone, gave a standard deviation of approximately 0.11 per cent sulfur. Thus, the presence of lithopone appears to cause somewhat poorer reproducibility of results by this method of analysis.

A study of the amounts of sulfur found by combustion, as listed in Table II, reveals systematic differences in evolved sulfur in the presence of different types of inorganic fillers. The lowest values of evolved sulfur are obtained in samples containing barium carbonate, group *C*. The values for the samples containing calcium carbonate (*B*), carbon black (*A*), and lithopone (*D*), exceeded those

found for the samples containing barium carbonate, on the average, by 0.18, 0.32, and 0.47 per cent, respectively. These differences in evolved sulfur are not appreciably influenced by the amount of added free sulfur.

Except for two of the compounds containing lithopone, the evolved sulfur is less than the added free sulfur. This fact, together with the observed differences in evolved sulfur for different fillers, can be interpreted in terms of varying degrees of combination of the added sulfur, exclusive of added inorganic sulfur, with the filler. Further evidence regarding this point is obtained from the study of the interaction between sulfur and fillers during combustion.

INTERACTION BETWEEN SULFUR AND FILLERS

Specimens from each of the rubber compounds were dissolved in hot *o*-dichlorobenzene[6], and the remaining inorganic residues were analyzed for total sulfur by the fusion method. Thus, the amount of inorganic sulfur formed during vulcanization was determined. Also the residues from the combustion of each vulcanizate were analyzed for sulfur by a wet oxidation procedure, ex-

TABLE III

INTERACTION BETWEEN SULFUR AND FILLERS DURING COMBUSTION

Compound	Inorganic sulfur added in compounding samples (%)			Sulfur found in residue (%)	
	Sulfide	Sulfate	Total	I[a]	II[b]
1*A*	0	0	0	0.00	0.16
2*A*	0	0	0	0.69	0.60
3*A*	0	0	0	0.01	0.02
4*A*	0	0	0	0.03	0.07
1*B*	0	0	0	0.02	0.30
2*B*	0	0	0	0.03	1.02
3*B*	0	0	0	0.01	0.12
4*B*	0	0	0	0.02	0.14
1*C*	0	0	0	0.01	0.29
2*C*	0	0	0	0.62	1.12
3*C*	0	0	0	0.01	0.27
4*C*	0	0	0	0.04	0.73
1*D*	3.10	3.05	6.15	6.15	2.92
2*D*	2.94	2.90	5.84	6.50	3.18
3*D*	3.05	3.01	6.06	6.13	2.84
4*D*	3.01	2.96	5.97	5.96	2.72

[a] Total sulfur determined in residue remaining after dissolving vulcanized rubber in *o*-dichlorobenzene.
[b] Sulfide sulfur in nonvolatile residue remaining from the combustion analysis. For group *C*, inorganic sulfur was determined by the fusion method.

cept in group *C*, where the fusion method was used. By comparing these two sets of values one can evaluate the degree of interaction between sulfur and fillers during combustion. These data are listed in Table III.

Examination of the values in column I leads to the conclusion that, except in compounds containing lead oxide, very little sulfur combines during vulcanization as inorganic sulfur. For compounds in batch 1, which were compounded with only 0.5 per cent of free sulfur, the formation of zinc sulfide during vulcanization did not occur to any appreciable extent. On the other hand, a comparison of the values in columns I and II indicates that sulfur combines to an appreciable extent during combustion with zinc, lead, calcium, and barium

compounds present in the vulcanizate. The largest amount of combination with the filler takes place in those samples containing lead oxide. When barium carbonate is present a moderate amount of combination takes place. The least combination occurs in samples which contain only carbon black, compounds 3*A* and 4*A*.

For compounds 1*D*, 3*D*, and 4*D*, which contain sulfide from the added lithopone, less sulfide is recovered after combustion than was present initially. The results for sulfur determined by the combustion method and listed in Table II

TABLE IV

COMPARISON OF VALUES FOR SULFUR FOUND BY DIFFERENT ANALYTICAL PROCEDURES

Compound	Sulfur added (%)				Sulfur found (%)			
	Free	Sulfide	Sulfate	Total	Fusion method	Zn + HNO_3 method	Combustion method + residue	Combustion method
1*A*	0.50	0	0	0.50	0.44	0.47	0.55	0.39
2*A*	2.50	0	0	2.50	2.53	2.36	2.27	1.67
3*A*	4.50	0	0	4.50	4.49	4.45	4.51	4.49
4*A*	6.50	0	0	6.50	6.41	6.39	6.42	6.35
1*B*	0.50	0	0	0.50	0.46	0.48	0.60	0.30
2*B*	2.50	0	0	2.50	2.43	2.26	2.54	1.52
3*B*	4.50	0	0	4.50	4.55	4.44	4.44	4.32
4*B*	6.50	0	0	6.50	6.50	6.36	6.33	6.19
1*C*	0.50	0	0	0.50	0.50	0.01	0.56	0.27
2*C*	2.50	0	0	2.50	2.55	0.01	2.57	1.45
3*C*	4.50	0	0	4.50	4.38	0.11	4.50	4.13
4*C*	6.50	0	0	6.50	6.59	1.40	6.50	5.77
1*D*	0.50	3.10	3.05	6.65	6.66	3.62	3.48	0.56
2*D*	2.50	2.94	2.90	8.34	8.33	5.27	5.17	1.99
3*D*	4.50	3.05	3.01	10.56	10.58	7.58	7.38	4.54
4*D*	6.50	3.01	2.96	12.47	12.14	9.39	9.11	6.39

show that these three samples evolved more sulfur than the corresponding samples of groups *A*, *B*, and *C*. Compounds 1*D* and 3*D* were the only two that evolved more sulfur than was originally added in the form of free and organic sulfur. These results indicate that inorganic sulfides liberate some sulfur during the combustion.

Compound 2*D* differs from the other members of group *D* in that more sulfide sulfur is found in the residue from combustion than was added in preparing the sample. Apparently the sulfur that combines with the lead more than compensates for that evolved from the lithopone.

COMPARISON OF METHODS

Table IV lists the sulfur added in compounding each sample and the amount of sulfur found by the three methods included in this study.

Specimens from each rubber compound were analyzed by the fusion method to determine the total sulfur present; by the zinc-nitric acid method to obtain a combined value for the free, organically bound, and sulfide sulfur; and by the combustion method to determine the sulfur evolved during combustion. In

the column headed Combustion method and residue, the results in Table II and those in column II of Table III have been combined.

In interpreting this table the following points should be borne in mind. For the compounds of groups *A* and *B*, which contained no barium, the values obtained by the fusion method, zinc-nitric acid method, and combustion plus residue procedure can be compared with the total amount of sulfur added. In the zinc-nitric acid method, the presence of barium carbonate leads to low and erroneous results as the barium sulfate formed during the oxidation phase of the analysis is not determined. The results of group *C* can be explained on this basis. For the compounds of this group, a comparison of the combustion plus residue values and those obtained by the fusion method can be made with the total amount of sulfur added, since no sulfate was added in preparing these samples. For the compounds of group *D*, both the zinc-nitric acid method and the combustion plus residue procedure determine all but the sulfate sulfur.

An analysis of the data shows that the fusion method is free of systematic errors and that its reproducibility is reflected by a standard deviation of 0.1 per cent sulfur. The zinc-nitric acid method, where applicable, tends to give results that are low, on the average, by 0.09 per cent sulfur. Its reproducibility is characterized by a standard deviation of 0.1 per cent sulfur, which is comparable to that of the fusion method. The values obtained by the combustion plus residue procedure appear to be free of systematic errors for the compounds of groups *A*, *B*, and *C*. For compounds of group *D* this procedure yields values which are consistently low (on the average, by 0.23 per cent sulfur), when compared to the sulfur added, exclusive of sulfate sulfur.

The values listed in the last column represent the sulfur evolved during combustion. Column II in Table III lists the inorganic sulfur formed during the course of the combustion. For the compounds of groups *B*, *C*, and *D*, where reaction takes place with the filler during combustion, the combustion method is only semiquantitative. Among the compounds of group *A*, samples 3*A* and 4*A* contained only carbon black as a filler, and satisfactory results were obtained by the combustion method for these samples. For samples 1*A*, and 2*A*, which contained zinc oxide and lead oxide, respectively, the combustion method yielded low results.

In conclusion, a value representative of the organically bound sulfur can be obtained by the combustion method for extracted samples that contain only carbon black as a filler and when zinc oxide and lead oxide are both absent. For the other samples, a combination of extraction, a total sulfur method and the *o*-dichlorobenzene solution procedure[6], appears to be required for determining organic sulfur reliably.

SUMMARY

A combustion method for rubber which determines the sulfur evolved at 480° to 500° C is compared with the fusion and the zinc-nitric acid methods. In the combustion method an interaction occurs between sulfur and fillers present in the rubber. The effect of particular fillers with respect to this interaction is discussed. A value representative of the organically bound sulfur in an extracted specimen can be obtained by the combustion method when no reaction takes place between the sulfur and the fillers during combustion. The fusion method yields results in good agreement with the total sulfur added in compounding the rubber samples. Except in the presence of barium compounds, the zinc-nitric acid method likewise determines total sulfur. When

barium compounds are present, barium sulfate is formed during the oxidation, and low values are obtained for the total sulfur.

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ABSORPTIOMETRIC MICRODETERMINATION OF TOTAL SULFUR IN RUBBER PRODUCTS *

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The literature contains numerous references to determination of total sulfur in rubber products as barium sulfate by gravimetric, volumetric, turbidimetric, or nephelometric methods. The latter methods were developed in the course of a search for a more rapid procedure than that afforded by standard gravimetric methods.

Recently an amperometric titration has been applied for the indirect semimicrodetermination of sulfur in organic compounds after precipitation as lead sulfate[1]. However, digestion of the sample in a sealed Carius tube has serious disadvantages for routine control of sulfur in rubber products, and the range of sulfur concentration (about 1 to 6 mg. of sulfur) recommended requires rubber samples of above 50 mg.

A new combustion apparatus for automatic determination of sulfur in steel has been applied successfully to rubber[2], but the cost of this single-purpose instrument precludes its use in most rubber laboratories.

Perchloric acid has been used to speed up oxidation of rubber products during determination of sulfur[3]. Published methods have all been for work on a macro-scale, where the possible explosion hazard has retarded general acceptance of this strong oxidant in routine analysis of rubber. Even with the more rapid oxidation provided by perchloric acid, the conventional gravimetric barium sulfate procedure is used to precipitate the sulfur. This limits the speed of analysis.

A very sensitive absorptiometric method for determining lead[4] depends on the strong selective ultraviolet light absorbance near 270 mμ of the lead chloride complex formed in strong hydrochloric acid solutions.

A rapid oxidation with nitric and perchloric acids on a safe micro-scale has been developed and is reported here. Sulfur is insolubilized and precipitated as lead sulfate with acetone. Absorptiometric measurement of lead as the lead chloride complex in 50 per cent hydrochloric acid provides data for calculating sulfur concentration.

EQUIPMENT, REAGENTS, AND PROCEDURE

Equipment.—Sample test-tubes, such as 15 × 100 mm. lipless culture tubes, of 12- to 15-ml. volume.

Capillary-tipped pipet connected to a water pump vacuum source. It may be made by drawing out the lower end of a standard pipet over a hot flame until it is of capillary size, with thin walls and an internal bore of 1 to 2 mm.

Standard high-speed semimicrocentrifuge capable of holding sample tubes.

Finger stall of pure gum rubber, or a finger from a rubber glove, extracted with a solution of 5% hydrochloric acid in acetone.

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Beckman DU quartz ultraviolet spectrophotometer with ultraviolet accessories, or a similar instrument.

Roller-Smith microbalance, torsion type, of 25-mg. capacity with V-shaped pan, or similar balance weighing to 0.01 mg.

Reagents.—Concentrated Nitric Acid-Bromine. Add reagent grade bromine to concentrated reagent grade nitric acid, in an all-glass dropper bottle with clean rubber or Tygon bulb. Have a layer of excess bromine on the bottom at all times.

Perchloric Acid, 70 to 72% reagent grade used as received. It is conveniently stored in an all-glass dropper bottle with either rubber or Tygon bulb. Store away from heat and handle only a small volume at a time, keeping the main part of the reagent in the original bottle in the storeroom. A 1-pound bottle is sufficient for over 2000 analyses.

Acetone, reagent grade. This must be redistilled if a brown residue is present after evaporation of the acetone following the precipitation and washing step.

Hydrochloric Acid, 50% by volume. A convenient method of preparation is to mix equal volumes of concentrated hydrochloric acid (35 to 38% reagent, specific gravity 1.1778 to 1.1923 range) and distilled water, using the same volumetric flask to measure the acid and water.

Lead Nitrate, 10%. Dissolve 10.0 grams of lead nitrate in water and dilute to 100 ml.

Calibration.—The average specific absorbance or K value (also termed absorptivity) of lead at 270 mμ is 54.0. The exact figure should be determined for each instrument for greatest accuracy.

Prepare a stock solution containing 1000 p.p.m. of lead by dissolving 0.160 gram of reagent grade lead nitrate in distilled water in a 100-ml. volumetric flask and diluting to volume. Pipet 10.0 ml. into a second 100-ml. volumetric flask and dilute to volume for a 100 p.p.m. lead standard. Use a 50-ml. buret to deliver different volumes between 0.5 and 8.0 ml. of the 100 p.p.m. standard into a clean glass Erlenmeyer flask. With a second 50-ml. buret, add enough distilled water to make exactly 10.0-ml. total volume of lead solution. Pipet 10.0 ml. of concentrated hydrochloric acid reagent into the flask. Shake well and measure absorbance of the 50% hydrochloric acid solution at 270 mμ in 1.00-cm. quartz sample cells. Calculate K_{Pb} as follows:

$$K_{Pb} = \frac{A_{270m\mu}}{b\,c}$$

where A is instrument absorbance at 270 mμ

b is internal cell thickness, and is neglected as long as it is 1.00 $\pm$ 0.005 cm.

c is concentration of lead in grams per liter at the dilution for which absorbance is measured—e.g., 100 p.p.m. $\times$ 4 ml./20 ml. = 20 p.p.m. or 0.020 gram per liter

The K value to be used is the average of the data over the range of linear instrument absorbance (usually considered 0.1 to 1.8 A).

Procedure.—Weigh 1 to 3 mg. of well milled representative sample. Sheet as thin as possible and weigh to 0.01 mg. on a suitable microbalance. Check the zero point of the balance carefully before and after any series of weighings. Brush the sample directly into the labeled sample tube, add 0.25 ml. of 10% lead nitrate solution from a 10-ml. buret, then add about 1 ml. of prepared con-

centrated nitric acid-bromine reagent and 3 drops (1 ml.) of 70% perchloric acid reagent. Do not add bumping stones of any kind.

Place a 3-inch square of sheet asbestos, about $\frac{1}{16}$ inch thick, on a hot plate at 300° to 320° C under a well ventilated hood. Immediately place a 150-ml. beaker containing as many as six sample tubes on the asbestos, and heat until completely oxidized (about 30 to 60 minutes). When the perchloric acid solution is essentially colorless and no particles of unoxidized sample are present on the walls of the tube (a trace of carbon black may be ignored), remove the beaker from the asbestos and place it directly on a bare hot plate at 300° to 320° C for about 10 minutes. The tube should fume copiously and the liquid condensation level should rise at least to within 0.5 inch of the top of the tube to be sure all lead nitrate is converted to lead perchlorate. Do not allow to dry; if this occurs, the sample may be recovered by fuming again with 2 drops of perchloric acid. As long as the residue is wet with liquid acid on cooling, no heat decomposition of lead perchlorate present should result. Lead perchlorate will decompose to form some acetone-insoluble lead chloride, if heated excessively in the absence of free perchloric acid.

Remove the beaker and tubes from the hot plate and place on a cool surface. If desired, accelerate cooling with a blast of compressed air. When tubes are at room temperature and cold to the touch (acetone poured into hot perchloric acid may result in a dangerous explosion), rapidly pour about 10 ml. of acetone reagent into all tubes in the beaker. Cover the index finger with a finger stall and stopper each tube. Shake just enough to mix acetone and acid residue. Lead sulfate will be present as a turbid suspension, but if only a trace of sulfur is present—e.g., 0.1%—this turbidity may not always be apparent. Always wipe the finger stall on edge of sample tube to minimize possible loss of a trace of sulfur.

Fill a 150-ml. beaker about two thirds full with hot water at 50° to 60° C, but not so hot that the acetone boils. Immediately immerse as many as six sample tubes in this water bath and let the beaker stand at room temperature for 10 to 15 minutes. Remove tubes from bath, and centrifuge in a semimicro-centrifuge for 1 to 2 minutes. Remove from centrifuge. With a capillary-tipped pipet connected by rubber tubing to a water pump vacuum draining down a sink, withdraw all but about 0.3 to 0.5 ml. of acetone from each tube. Always hold the tube in a vertical position, and lower the pipet tip in the center of the tube. Be careful not to jar the tube when removing it from the centrifuge. Wash the precipitated lead sulfate twice more with about 10 ml. of acetone, centrifuging 1 to 2 minutes each time. Three of these small tubes may conveniently be handled at the same time during the washing operation when acetone is drawn off and added.

After removal of the third addition of acetone, add 2 drops of water to each tube and place the beaker with tubes on the 300° C hot plate to evaporate to dryness. Reduce the temperature if bumping occurs, but complete drying at high temperature for 5 to 10 minutes. Acetone absorbs in the ultraviolet and must be removed completely. When dry, remove from the hot plate, and cool in an air blast. The residue should be white at this point. If any trace of brown coloration is apparent, heat the tubes with the beaker at 550° C for 15 minutes until the residue is white. Then proceed as usual.

When tubes are cool, carefully pipet 10.0 ml. of exactly 50% hydrochloric acid reagent into the sample tubes. With a finger stall over the finger to act as a stopper, shake the tubes a few seconds until all the lead sulfate is in solution. Inspect the bottom of the tube for undissolved material. If there is difficulty

in dissolving the precipitate (or if white side-wall stock with acid-insoluble titanium dioxide is being analyzed), add a few small silicon carbide bumping stones and shake vigorously. In the case of white side-wall stock, or other material where acid-insoluble matter is present, centrifuge the sample to throw down the acid-insoluble material.

Sometime during this solution operation, place the Beckman DU spectrophotometer in operation with the hydrogen tube. An instrument slit width of about 1.1 mm. with sensitivity set near the middle of its range has proved satisfactory. Rinse a 1.00 ± 0.005-cm. quartz sample cell twice with about 2 ml., and finally pour in 3 to 4 ml. of the sample solution. Record absorbance at 270.0 mμ against a 50% hydrochloric acid blank. If absorbance is above 1.80, pour the contents of the cell into a 10-ml. glass-stoppered graduated cylinder and dilute to twice its volume accurately with 50% acid (a 1:1 dilution).

Calculate the per cent sulfur in the sample as follows, with a spectrophotometer cell thickness of 1.00 cm. A reagent blank normally amounts to about 0.010 absorbance or less, which is about 0.01 to 0.02% sulfur. Therefore, the experienced analyst may neglect the reagent blank, except for the most exacting work.

$$\% \text{ sulfur} = \left[\frac{A \times \frac{\text{S}(32.07)}{\text{Pb}(207.2)} \times 100}{K_{\text{Pb}} \times c \text{ (mg./ml.)}} \right] = \frac{A_{270\text{m}\mu} \times 0.155 \times 100}{54.0 \times \text{(wt. mg./10 ml. acid)}}$$

For 10.0 ml. of acid this reduces to

$$\% \text{ sulfur} = \frac{(2.87)\, A_{270\text{m}\mu}}{\text{mg. of sample}}$$

If 1:1 volume dilution is necessary (20-ml. volume), the factor is doubled and is 5.74.

EXPERIMENTAL WORK

Evaluation of the procedure for sample preparation used for semimicro-amperometric titration[5] proved that the amount of residual nitric acid was a critical point in working on a microscale with low-sulfur compounds. A significant amount of lead sulfate is dissolved by the residual nitric acid.

Use of potassium chlorate on a micro-scale, following the conventional ASTM macro-method[6], oxidized the sample completely in 5 to 10 minutes. However, it proved too unreliable for routine analysis, since excess lead nitrate, excess acid, degree of dryness of residue, and washing technique were critical.

Use of perchloric acid was investigated as a final resort. Even this gave erratic results until the precipitation technique with an organic solvent was developed. This proved the answer to the recovery problem.

High and erratic results may be obtained if fuming sulfuric acid is near when the sulfur is being determined.

Oxidation.—The oxidation is carried out in the presence of excess lead nitrate. Normally about 10 mg. is sufficient for up to 5 mg. of rubber stocks, but about 25 mg. is added to ensure complete precipitation of sulfur as lead sulfate for diverse materials. It is convenient to add the lead nitrate from solution; the consistent amount added in this manner tends to result in more accurate data and to give a more reproducible blank.

Oxidation of natural rubber with fuming nitric acid is almost instantaneous and violent, and may lead to loss of sulfur. Consequently, the more slowly

acting concentrated acid is used for all elastomers and other materials. Though concentrated nitric acid will not decompose Butyl stocks, this elastomer and similar hard-to-oxidize materials are oxidized completely when the high boiling (200° C) perchloric acid content increases as the nitric acid evaporates. As long as analyses are carried out on a micro-scale, this is a safe practice, but larger samples of Butyl polymer, e.g., 100 mg., may oxidize with explosive violence, once perchloric acid becomes concentrated by evaporation, unless fuming nitric acid is first used to decompose the polymer. Perchloric acid should never be used indiscriminately for oxidation purposes.

The heavy bromine gas retains and oxidizes volatile sulfur compounds formed in the initial stages of oxidation. Though it has been said that iodic acid is superior to bromine for this purpose[3], the amount of sulfur lost when bromine is used in the presence of excess lead nitrate has proved negligible for routine analysis of rubber products and compounding materials.

Unless perchloric acid volume is above 2 drops, incomplete oxidation of sulfur may result in some cases. A range of 3 to 5 drops of added perchloric acid gave essentially the same sulfur recovery with natural rubber stocks but in some cases use of 5 drops gave somewhat lower recoveries, e.g., 95 to 98 per cent of 3-drop recovery. Safety precautions, as well as lead sulfate solubility, require use of the minimum volume that will produce complete oxidation, which is about 3 drops (0.1 ml.).

The only really critical point about oxidation with the specified amount of perchloric acid on a micro-scale is possible evaporation to dryness. In such a case the heat-sensitive lead perchlorate present decomposes to form lead chloride, which is insoluble in acetone and will lead to false high figures for sulfur recovery. The sample may be recovered by reheating to fumes with 2 drops of perchloric acid.

Precipitation.—Perchlorates of most cations are soluble in alcohol and acetone. Potassium perchlorate is the only salt essentially insoluble in these solvents[4]. The precipitation of lead sulfate through its insolubility in organic solvents offered a novel means of separation from interfering perchlorate salts. Several other solvents were investigated, including water-miscible alcohols (ethanol and methanol), higher ketones (methylethyl ketone and methylisobutyl ketone) and ether (dioxane) alone, as well as water-immiscible hydrocarbons (*n*-hexane) mixed with acetone.

When 3 drops of perchloric acid were used, the alcohols all gave low recoveries, on the order of 60 to 90 per cent of that of reagent grade acetone. The acid in dioxane dissolved practically all the lead sulfate. Methylethyl ketone gave recoveries only a little lower than acetone, but methylisobutyl ketone precipitated lead salts other than lead sulfate in the second wash, once acid concentration was reduced by the first wash. Mixtures of hydrocarbons and acetone offered no advantage over acetone alone.

Early work with acetone was carried out with specially prepared essentially anhydrous acetone. However, it was later proved that, though the water content of the acetone must be controlled, reagent grade acetone can be used. In fact, 1 to 2 per cent of water added to reagent grade acetone may at times be beneficial. The presence of a trace of water inhibits the oxidation of anhydrous and reagent grade acetone, which normally results in development of a yellow coloration as the acetone stands in the presence of perchloric acid. However, this solvent oxidation does not normally appear to affect the quantitative recovery.

When acetone is first poured into the residual cold perchloric acid after

sample digestion, an exothermic reaction results due to heat of solution. This has not proved hazardous even with such a large excess as 20 drops of perchloric acid, which would mean a final concentration of about 10 per cent perchloric acid in acetone. On the micro-scale involved, only 2 drops (0.07 ml.) of excess perchloric acid are diluted to about 8 ml., which is a concentration of less than 1 per cent perchloric in acetone. Consequently it is felt that no hazard is involved in adding acetone to cold perchloric acid, as done here on a micro scale.

Paradoxically, heating the acetone in hot water at below the boiling point tends to force complete precipitation more efficiently than cooling in an ice bath. With high-sulfur materials, the additional recovery due to heating the acetone may not always be apparent, and immediate centrifuging may be justified in many cases. However, a definite increase in sulfur recovery was noted on several occasions following a period of heating the acetone, particularly with Butyl stocks, so this step is incorporated in the procedure. Heating a reagent blank in the same manner for extended periods did not alter the blank. Therefore, such heating does not decompose the acetone-soluble perchlorate salts.

Interferences.—Lead and iron salts and even barium perchlorate are very soluble in acetone and are probably all dissolved when the first acetone is added to precipitate the insoluble lead sulfate (the sulfur could be precipitated as barium sulfate in the same manner with excess barium chloride). However, a residual volume of about 0.5 ml. remains in the tube each time after the clear acetone is drawn off following centrifuging. This makes necessary two more dilutions of the residue to reduce the blank to negligible proportions. A correction for background absorbance was necessary when potassium chlorate or nitric acid alone was used as the oxidant, but the acetone solubility of interfering perchlorates eliminates all possible interference. Even lead present in a stock as the hard-to-dissolve oxide, and acid-insoluble barium sulfate will be converted to perchlorates and be removed by the acetone with quantitative recovery of sulfur as lead sulfate.

This procedure offers a sensitive and rapid method for determining lead in rubber products and compounding materials. The sample is wet or dry ashed, then taken up in 50 per cent hydrochloric acid. The absorbance at 270 mμ is measured and per cent lead is calculated using a specific absorbance, K, of 54.0. A simple mathematical correction may be made for any background interference due to iron.

Acetone absorbs strongly in the ultraviolet spectral region of interest and must be removed completely by evaporation before the 50 per cent acid is added. Some lots of reagent-grade acetone had to be redistilled, since they left a brown residue when the acetone was evaporated to dryness after the final wash. This residue absorbs and gives high results for sulfur. The brown material was apparently a high boiling oxidized impurity formed by oxidation with perchloric acid. It could be removed by heating the sample tubes at 550° C for 15 minutes. However, it is best eliminated by redistilling the reagent-grade acetone to ensure purity. Addition of 2 drops of water to each sample before evaporation to dryness will reduce such interference.

Standard micro-chemical practice would call for use of a filter stick or some method of filtration for each sample, but the vacuum pipet is much faster and easier to handle. Recoveries are some times a little low, e.g., 98 per cent of theory, for inorganic salts where no sulfur is likely to be lost by oxidation. This may be attributed to the slight solubility of lead sulfate in the acidic acetone.

Solution.—It has been shown[7] that the intensity and selectivity of ultraviolet absorbance of lead in aqueous hydrochloric acid change drastically with

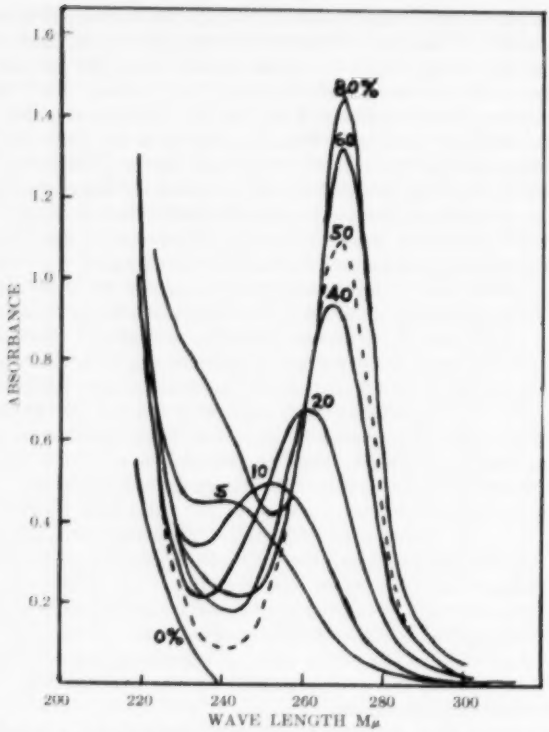

FIG. 1.—Effect of acid concentration on absorbance of lead. 20 p.p.m. lead. Range 0 to 80% HCl. - - - 50% HCl.

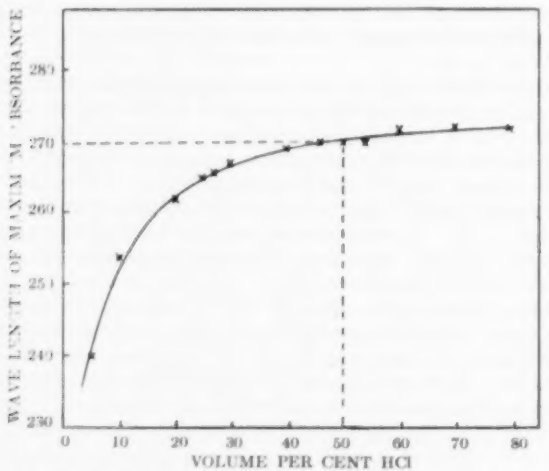

FIG. 2.—Shift of absorbance maximum with acid concentration.

change in acid concentration. This was investigated, and the data are illustrated in Figure 1. The maximum is sharp and symmetrical at an acid conscentration above about 40 per cent.

The shift of wave length of maximum absorbance toward longer wave lengths is observed in Figure 2 to be an asymptotic function of the acid concentration. Above about 40 per cent acid the shift in wave length is slow, and at 50 per cent acid concentration the wave length of the maximum (270 mμ) will be essentially constant. Its location will not be affected by small changes in acid concentration, which may occur, owing to normal variation in normality of the concentrated reagent grade hydrochloric acid used.

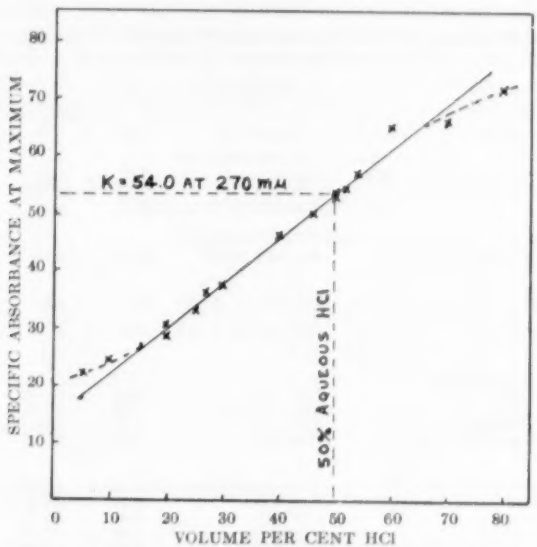

FIG. 3.—Effect of acid concentration on specific absorbance of lead. 20 p.p.m. lead.

Figure 3 shows that the intensity of absorbance, or specific absorbance, K at the maximum is a linear function of acid concentration in the range of about 20 to 60 volume per cent hydrochloric acid. The K value of 50 per cent acid is 54.0 at 270 mμ, but in 25 per cent acid it drops to 34.0 at 264 mμ. The high (50 per cent) acid concentration is preferred, because the greater sensitivity makes possible a smaller sample, which is rapidly oxidized with a minimum amount of perchloric acid, and any interfering absorbance is reduced in relative intensity to negligible proportions by the strong lead absorbance. Use of a weaker acid, e.g., 25 per cent, may prove advantageous for purified materials of high sulfur content. However, dilution to larger volumes of 50 per cent acid than the 10 ml. used here is preferred because of the greater accuracy possible at high sensitivity.

The concentrated ($12N$) hydrochloric acid (considered 37 per cent hydrochloric acid with a range of 35 to 38 per cent) as used to prepare a 50 per cent acid mixture by volume would result in a range of 17.5 to 19 per cent hydrochloric acid content in a 1:1 mixture. During development of the procedure,

no abnormal results were obtained which could be attributed to variations of hydrochloric acid concentration. For determination of sulfur in rubber products, no correction was made for variation of hydrochloric acid content of the concentrated acid. For the most accurate work, the hydrochloric acid content should be checked carefully and kept constant.

Any chemically inert material can be used as a finger stall for stoppering the sample tubes containing acid. Rubber provides a better seal for acetone washing, but polyethylene film is satisfactory for 50 per cent aqueous acid. Pure-gum rubber is satisfactory for both acetone and acid, if extracted with both solvents before use. However, any possibility that acid will extract iron from

TABLE I

DETERMINATION OF ORGANIC AND INORGANIC SULFUR IN RUBBER COMPOUNDING MATERIALS

Compounding material	Sulfur (%) Theoretical	By analysis	Av.	Mean deviation (%)	Recovery (% of theory)
Inorganic sulfur compounds					
Sodium sulfate	22.6	21.8, 22.0	21.9	±0.1	97
Zinc oxide		0.30, 0.34	0.32	±0.02	
Barium sulfate	13.7	13.4, 13.1	13.2	±0.2	96.5
Organic sulfur compounds					
Sulfur (commercial rubber grade)	99.5	96.2, 99.4, 98, 100	98.4	±1.3	99 (97-101)
Accelerators					
MBTS (purified)[a]	38.6	36.2, 36.4, 37.9, 38.5	37.3	±0.9	96.7 (94-100)
TMTD (purified)[b]	53.4[c]	54.0, 52.6, 54.8, 53.4 52.0	53.4	±0.8	100 (97-103)
Softeners					
Petroleum oils (rubber grade)					
1.39% by O_2 bomb		1.40, 1.28	1.34	±0.06	
0.20% by O_2 bomb		0.11, 0.13, 0.13	0.13	±0.01	
Coal tar origin (Bardol)		0.57, 0.64	0.60	±0.04	
Asphalt origin (Paraflux)		0.86, 0.80	0.83	±0.03	
Carbon blacks					
SRF (furnace)		0.044, 0.043, 0.064	0.050	±0.009	
HMF (furnace)		0.12, 0.14	0.13	±0.01	
FEF (furnace)		0.67, 0.64	0.66	±0.02	
HAF (furnace)		0.29, 0.35	0.32	±0.03	
SAF (furnace)		0.47, 0.45	0.46	±0.01	
EPC (channel)		0.15, 017	0.16	±0.01	

[a] Benzothiazolyl disulfide.
[b] Tetramethylthiuram disulfide.
[c] Chemical analysis by ASTM procedure gave 51.8, 51.5, and 52.9% sulfur in TMTD, average recovery of 97.7%.

compounded rubber must be avoided, since ferric chloride absorbs in the ultraviolet. The uncovered finger should never be used to stopper the sample tubes, whether acetone or acid is the solvent. Safety preparations for handling lead recommended that the analyst wash his hands thoroughly after determining total sulfur by this method.

APPLICATIONS

The results obtained by the perchloric acid method represent true total sulfur, and are comparable to those by the sodium carbonate fusion method[5]. Only in critical work, or in application to materials other than rubber products, need possible loss of volatile sulfur be taken into consideration.

The results are not strictly comparable to those of the standard ASTM gravimetric method, since perchloric acid will recover sulfur from barium sul-

fate, which is filtered off as acid-insoluble in the regular method. Both methods determine sulfur in acid-soluble inorganic sulfates, such as sodium and calcium sulfates. The combustion method does not determine inorganic sulfate, as does this wet oxidation procedure.

If there is need to distinguish between inorganic and organic sulfur, the material can be ashed prior to determination of sulfur by wet oxidation on the ash. However, for the normal tire and tube stock, results are also in close agreement with the standard gravimetric barium sulfate procedure following nitric acid oxidation.

Analyses in rubber chemistry.—The data of Table I illustrate the wide application of the perchloric acid method to both inorganic and organic rubber compounding materials. The following modifications of the regular perchloric acid procedure for analysis of these compounding materials are recommended.

Carbon Black. Weigh 5 to 10 mg. of pelletized black and digest with a minimum amount of perchloric acid (3 to 5 drops). Add 3 drops, and if oxidation is incomplete, add 1 or 2 more as required for a colorless wet residue.

TABLE II

TOTAL SULFUR IN COMPOUNDED RUBBER STOCKS BY ABSORPTIOMETRIC METHOD

Stock type	Polymer type	Gravimetric sulfur (%) Range	Gravimetric sulfur (%) Av.	Absorptiometric sulfur (%) Range	Absorptiometric sulfur (%) Av.	Mean deviation (%)	Recovery* (%)
Standard	GR-S	1.28 to 1.34	1.31	1.28 to 1.38	1.32	±0.04	101
Standard	Natural	2.05 to 2.12	2.08	2.12 to 2.19	2.16	±0.04	104
Tire tread	Natural		1.72	1.85 to 1.93	1.89	±0.03	110
Foam rubber	Natural		2.62	2.52 to 2.61	2.56	±0.03	98
White side wall	Natural		2.02	1.91 to 1.98	1.95	±0.02	97
Tire tread	Mixed GR-S and natural		2.18	2.14 to 2.15	2.15	±0.01	99
Tire tread	GR-S (LTP)		1.53	1.50 to 1.57	1.54	±0.04	100
Hose (10% $CaCO_3$)	Neoprene		0.60	0.59 to 0.68	0.62	±0.04	103
Cement	Chlorinated rubber		0.66	0.72 to 0.80	0.76	±0.03	115

* % recovery by absorptiometric method relative to recovery by ASTM gravimetric method, % absorptiometrically × 100/% gravimetrically.

Inorganic Salts. For high-sulfur salts, such as barium sulfate, weigh 1 to 2 mg. and digest with 3 drops of perchloric acid. Dilute to 25 to 100 ml. with 50% hydrochloric acid as needed. For low-sulfur inorganic salts, such as zinc oxide, make the final 50% acid volume up to 10 ml. as usual.

Petroleum Oils (rubber grade, essentially nonvolatile at 100° C). Weigh 5 to 10 mg. (1 small drop) and digest with a minimum amount of perchloric acid (3 to 5 drops). Dilute to 10 ml. with 50% acid, with further dilution as needed for high-sulfur oils. Weighing of softener oils on a microbalance is facilitated by taking up the sample on a weighed cotton cord, cutting off the part of the cord with the sample, and dropping the cord and all into a sample tube. The cord must be essentially sulfur-free.

Organic Compounds. For sulfur below 3%, proceed as for rubber analysis. For high sulfur, such as tetramethylthiuram disulfide accelerator, dissolve 1 to 5 mg. in 100 ml. of chloroform or other suitable solvent. Pipet an aliquot of 1 to 5 ml. into a sample tube and evaporate just to dryness at low temperature (70° C oven or water bath). Proceed as for rubber analysis, and include the dilutions of the chloroform solution in the final calculations. Alternatively, the final acid volume can be made up to 100 ml. instead of 10 ml.

The data of Table II illustrate the application of the method to a wide

variety of complex compounded rubber products. No difficulty was experienced in analysis of natural, GR-S, Butyl, Neoprene, or chlorinated rubber-base polymer stocks. Insolubility of titanium dioxide in white side-wall tire stock requires an extra centrifugation, to remove turbidity, but no other modification was necessary for any stock analyzed.

Other methods of measurement.—The amount of lead sulfate precipitate can be measured in different ways—polarographic, volumetric, gravimetric, turbidimetric, or nephelometric techniques. The volumetric technique might involve the well known, but difficult, visual end-point titration with tetrahy-

TABLE III

GRAVIMETRIC SULFUR AS LEAD SULFATE BY PERCHLORIC ACID OXIDATION SEMIMICROMETHOD

Stock	Sulfur theoretical (%)	S by $BaSO_4$ (ASTM) (%)	Gravimetric lead sulfate: Sample (mg.)	Gravimetric lead sulfate: $PbSO_4$ (mg.)	Gravimetric lead sulfate: Sulfur (%)	Recovery (% of theoretical)
Compounded elastomer stocks						
Natural tire tread	2.14	2.08 (2.05 to 2.12)	75.0	15.3	2.16	97.2
			100.8	19.1	2.01	
					Av. 2.08	
GR-S tire tread	1.26	1.31 (1.28 to 1.34)	104.7	12.6	1.27	103
			92.6	11.6	1.33	
					Av. 1.30	
Butyl tube	1.38	1.35	112.4	13.4	1.27[a]	89
			92.8	10.9	1.24[a]	
			102.0	11.2	1.17	
			97.2	11.5	1.25	
					Av. 1.23	
Elastomer compounding materials						
MBTS (purified)	38.6		2.82	10.1	37.9	95
			5.24	17.9	36.2	
			10.19	34.6	36.0	
					Av. 36.7	
TMTD (purified)	53.4	51.5	2.42	12.1	53.0	98.6
		52.9	5.03	24.8	52.2	
		51.8				
					Av. 52.6	
		Av. 52.1				
Sulfur (commercial of high purity)	100	—	2.68	26.1	103	101
			4.56	43.1	100	
			4.95	47.4	101	
			2.29	22.8	105	
			2.17	20.8	101	
			3.22	29.6	98	
					Av. 101	

[a] Analysis was completed even though these two of four samples showed explosive oxidation near end of oxidation. Explosive oxidation occurred because of failure to swell samples in chloroform as final procedure for Butyl requires.

droquinone indicator, or amperometric titration[6]. However, the ultraviolet absorptiometric procedure is considered equal or superior in accuracy and reliability to any of these methods. In addition, its high sensitivity makes possible analyses on a micro scale.

It was desired to demonstrate that the procedure for sample preparation with perchloric acid and acetone could be used to advantage with other methods of measurement. Results of a gravimetric semimicroprocedure are given in Table III. Some modifications were necessary for the gravimetric method. Sample size ranged from 5 to 10 mg. for high-sulfur compounds and from about 75 to 100 mg. for low-sulfur compounded rubber products. Sulfur content was kept below 5 mg., which means a weighable lead sulfate recovery below 50 mg.

Amount of reagent per sample was increased to 100 mg. of lead nitrate and 1 to 2 ml. of concentrated nitric acid, followed by 3 or 4 ml. of fuming nitric acid added in two or three treatments. Perchloric acid was added up to 10 drops for organic compounds containing no carbon black; and up to 20 drops for compounded rubber stocks. Volume of acetone wash was maintained at about 10 ml. per wash, but four washes were used.

Close attention to complete disintegration of rubber products with fuming nitric acid prior to addition of perchloric acid is essential. No trouble was encountered with perchloric acid oxidation of natural and GR-S rubber stocks. However, the relatively large (100 mg.) sample of hard-to-oxidize Butyl rubber may oxidize with explosive violence unless completely disintegrated before the nitric acid has evaporated. A preliminary swelling in chloroform and evaporation of the chloroform prior to acid treatment were used to speed oxidation of Butyl rubber in nitric acid.

If a significant amount of acid-insoluble material from the sample is present, it is necessary to dissolve the lead sulfate in 50 per cent hydrochloric acid, centrifuge, and weigh the sample tube again to correct for the acid-insoluble. No correction was made for any trace of acid-insoluble material in the data of Table III. Absence of any significant turbidity after dissolving the lead sulfate will show where such a correction is unnecessary.

Petroleum chemistry.—The general application of this method to fields other than rubber chemistry is suggested by successful analysis of petroleum oil softeners. The somewhat lower results obtained may indicate the presence of volatile sulfur compounds, but agreement of the perchloric acid and oxygen bomb methods is close enough to make the wet oxidation satisfactory for routine analyses. Regular analysis by oxygen-bomb methods could be speeded by using lead nitrate and measuring the lead sulfate formed by the absorptiometric method outlined here. For critical analyses where volatile materials are concerned, the sample may be oxidized by the Carius sealed tube method in the presence of lead nitrate. Perchloric acid is then added when the tube is opened and the regular procedure outlined here is followed thereafter.

Absolute structural analyses.—The method appears to be of value for absolute determination of sulfur content in securing data for chemical formula reconstruction. Analysis of purified tetramethylthiuram disulfide and high purity sulfur shows an average of 99 to 100 per cent recovery. The perchloric acid procedure outlined here has been simplified for rapid routine determination of sulfur, and some precision and accuracy have been sacrificed to speed up the analysis. Modifications, such as a somewhat larger sample with 100 ml. or more of exactly 50 per cent acid, should make the accuracy comparable to that of other methods now in use. A preliminary slow oxidation with nitric acid and excess bromine at room temperature prior to heating, or use of conventional Carius or bomb techniques, should eliminate loss of trace amounts of volatile sulfur compounds.

Accuracy.—The accuracy is difficult to prove in analysis of rubber products because sulfur is present in several compounding materials (see Table I). To prepare a standard stock of known true total sulfur content would require a prohibitive amount of work, involving determination of sulfur in every material added to the stock. However, a practical alternative is to consider only added sulfur as such and that present in accelerators added, in calculating theoretical percentage sulfur. Analysis of data of Table IV indicated the absorptiometric method recovers 97 to 108 per cent of theoretical. This is good, considering the many factors affecting the theoretical per cent sulfur.

Precision.—The data of Table IV illustrate the precision of the absorptiometric micromethod for analysis of three complex compounded cured rubber stocks. Work of seven different analysts, most of them unfamiliar with the new technique, shows a mean deviation from average of ±0.06 per cent for the

TABLE IV

PRECISION AND RELATIVE ACCURACY OF ABSORPTIOMETRIC MICROMETHOD

Analyst		Sulfur found (%) Natural	GR-S	Butyl
1		2.10	1.40	1.30
		2.06		1.36
	Av.	2.08		1.33
2		2.10	1.29	1.38
		2.06	1.33	1.43
		2.09	1.29	1.35
	Av.	2.08	1.30	1.39
3		2.19	1.27	1.46
		2.25	1.39	1.43
			1.39	
	Av.	2.22	1.35	1.44
4		2.10	1.46	—
		2.15	1.26	
	Av.	2.12	1.36	
5		2.12	1.39	1.34
		2.12	1.35	1.37
	Av.	2.12	1.37	1.36
6		2.01	—	1.20
		2.04		1.16
	Av.	2.03		1.18
7		1.88	1.39	1.38
		1.94	1.38	1.35
	Av.	1.91	1.38	1.36
Summary of data				
Av. for sample (%)		2.09	1.36	1.34
Max. deviation		−0.18	−0.06	−0.16
Mean deviation		±0.06	±0.02	±0.06
Comparison of ASTM gravimetric and absorptiometric methods				
Av. absorptiometric S (%)		2.09	1.36	1.34
Theoretical S as compounded (%)		2.14	1.26	1.38
Av. gravimetric S (%)		2.04	1.31	—
Ratio $\frac{\text{absorptiometric S (\%)}}{\text{theoretical S (\%)}}$		0.98	1.08	0.97
Ratio $\frac{\text{absorptiometric S (\%)}}{\text{gravimetric S (\%)}}$		1.02	1.04	—

natural and Butyl stock and only ±0.02 per cent for the GR-S stock. Familiarity with the procedure should give duplicate determinations that check well within ±0.1 per cent deviation for analysis of rubber products.

Absolute accuracy is here best measured by determination of sulfur on purified organic and inorganic materials. Recoveries of 97 per cent or higher of available sulfur in pure compounds are observed in Table I. Similar or higher recoveries are obtained for organic compared to inorganic compounds, which indicates there is probably no loss of sulfur through volatilization of the organic material. The slightly low recoveries for these pure materials may be attributable to a very slight solubility of lead sulfate in perchloric acid in the presence of acetone. The absorptiometric recovery is a little higher than the gravimetric recovery for both rubber stocks and purified tetramethylthiuram disulfide accelerator.

A more practical basis for establishing accuracy is to determine relative accuracy by comparing recoveries for the same sample by the conventional gravimetric and absorptiometric methods. This was done for the GR-S and natural-rubber stocks of Table IV. Average recoveries by the gravimetric method are about 97 per cent of those by the absorptiometric method. However, agreement of the results is so close that the two methods may be considered of comparable accuracy for all practical purposes.

DISCUSSION

The only special equipment required for this analysis is an ultraviolet spectrophotometer capable of making absorbance readings at 270 mμ. The Beckman DU spectrophotometer used here is by no means a single-purpose instrument in the rubber laboratory. Its application to identification of accelerators[5] and antioxidants[9] and for quantitative determination of accelerators[6] has been described. All other equipment and reagents are standard equipment in the average rubber control laboratory.

The method has all the advantages of a micromethod, but eliminates most of the disadvantages involving tedious manipulation. Work on a micro-scale makes possible a significant saving in time, cost of glassware, and amount of reagents required. Volume of oxidizing reagents is here measured in drops, rather than milliliters, as in the macro-method. This micro-method is sensitive to contaminants, and glassware should be kept scrupulously clean and stored protected from laboratory dust.

The sample size is so small that the rubber chemist may often question the homogeneity of the sample. However, rubber is one of the best dispersing mediums known, and under normal conditions after cured stocks have been milled the homogeneity has never proved a problem. On the other hand, the sample can be so minute that the method may be used to detect incomplete dispersion of sulfur of sulfur-bearing materials in rubber products, when it is not homogenized on a mill.

The method is considerably more rapid than any conventional procedure used for determination of sulfur in rubber products. An experienced analyst can complete an analysis in duplicate in about 2 hours, with less than 1-hour working time. Several samples may be conveniently run simultaneously with only a nominal increase in total time for analysis. In the rubber industry there is normally no need for a total sulfur procedure that will yield results in less than 3 to 4 hours. Therefore, this method is a practical solution to the long-

standing problem of a more convenient and rapid determination of total sulfur in rubber products.

SUMMARY

The 1.0 to 2.5 per cent of sulfur normally present in rubber products is oxidized with concentrated nitric acid-bromine reagent, followed by perchloric acid in the presence of excess lead nitrate. Sulfur as lead sulfate is precipitated and washed with acetone. The lead sulfate is dissolved in 50 per cent hydrochloric acid, and absorbance of the lead chloride complex is recorded at 270 mμ. Sulfur is calculated on the basis of the measured lead content of the precipitate. The high sensitivity puts the method in the micro-range. An experienced analyst can analyze 40 to 50 samples a day. Precision and accuracy are comparable to those of the conventional barium sulfate gravimetric method at the low sulfur concentrations normally found in rubber products.

ACKNOWLEDGMENT

The author acknowledges the help of J. Z. Falcon with development work. His interest in perchloric acid as an oxidant aided materially in developing the final procedure.

Many analysts of the Firestone analytical laboratories helped to determine the precision of the method and obtained data on its application to diverse rubber compounding materials. The greater part of the gravimetric barium sulfate data in tables was secured by R. O. Lankenau.

The permission of the Firestone Tire and Rubber Company to publish this paper is gratefully acknowledged.

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IDENTIFICATION OF ACCELERATORS AND ANTIOXIDANTS IN COMPOUNDED RUBBER PRODUCTS *

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The identification of rubber compounding ingredients in the past has been accomplished mainly through the use of color reactions[1]. Recently these identifications have been made more positive through the use of chromatographic separation techniques[2] and characterization by ultraviolet[3] and infrared[4] spectrophotometry. Parker and Berriman[5] have recently published an excellent comprehensive study of the chromatographic determination of accelerators and antioxidants in vulcanized rubber, including data on many of the accelerators and antioxidants which are widely used today. A complete characterization of the composition of an unknown vulcanizate necessitates a detailed knowledge of the chromatographic behavior, not only of all the commercially used accelerators and antioxidants, but also of their decomposition products which are produced during vulcanization. Therefore, considerable background experience is necessary before the chromatographic technique can be used successfully.

The tendency of accelerators to decompose or react during mixing, vulcanization, or extraction has plagued many analysts in the past and has resulted in loss of accelerators, or their conversion to other chemical compounds. Examples of some of the difficulties which have been encountered are given below. Parker and Berriman[5] have shown that stearic acid interferes with the detection of bis(dimethylthiocarbamoyl) disulfide (Methyl Tuads) in vulcanized rubber. Similarly, diethylthiocarbamoyl disulfide (Ethyl Tuads) and dimethylthiocarbamoyl sulfide (Monex) could not be detected by these investigators after vulcanization. The conversion of dimethylthiocarbamoyl disulfide to zinc dimethyldithiocarbamate (Methyl Zimate) in the presence of zinc oxide during vulcanization has been observed by Dufraisse and Jarrijon[6], Mann[4], and others[7].

Mann[4] states that he was unable to detect either the piperidine salt of 1-piperidinecarbodithioic acid (Pip-Pip) or zinc pentamethylenedithiocarbamate (Pipazate) in vulcanizates where the former was used as an accelerator. Mann[4] has also observed that *N*-cyclohexyl-2-benzothiazolesulfenamide (Santocure) is converted to 2-mercaptobenzothiazole (MBT) during vulcanization. The cyclohexylamine fragment of the molecule could not be found after vulcanization.

Dufraisse and Houpillart[8] identified both 2-mercaptobenzothiazole and 2,2′-dithiobisbenzothiazole (MBTS) in vulcanized rubber compounds which originally contained only one of these accelerators. They failed to detect diphenylguanidine (DPG) in acetone extracts of vulcanized rubber compounds accelerated with diphenylguanidine[8].

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The procedure proposed here simplifies these problems by using an extraction technique which promotes decomposition of the accelerators and collects the fragments obtained.

A perusal of the accelerators commonly used in rubber compounding shows that all contain one or more of the following components: a thiazole (or related compound), an amine, a guanidine, and carbon disulfide. The proposed procedure isolates and identifies each of these components, along with the amine

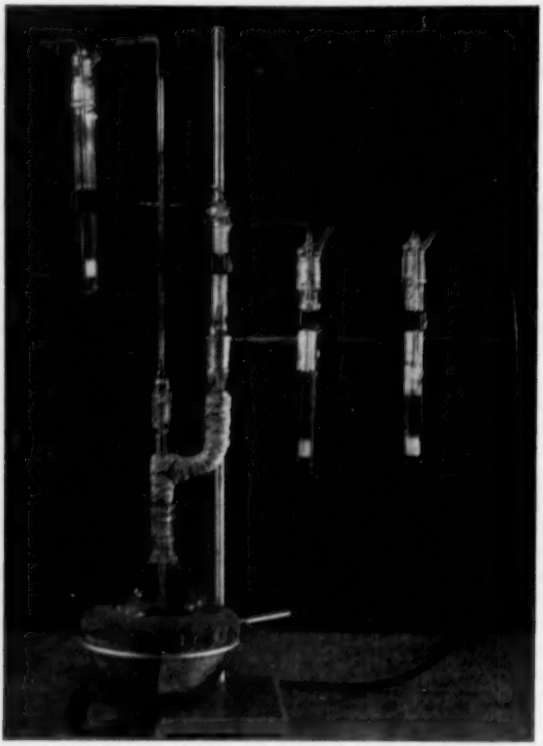


FIG. 1.—Apparatus for extractive decomposition of rubber compounding materials.

antioxidant used. The accelerator which was present in the rubber compound can then be determined, in most instances, from a knowledge of the fragments obtained from known accelerators.

Consequently, many of the difficulties encountered by previous investigators are eliminated. Easily decomposed accelerators can be classified or identified, since the analytical scheme is designed primarily to isolate and identify the decomposition products and not the original accelerators.

The extraction medium must not only promote the accelerator decomposition, but it must also be efficient in extracting the decomposed fragments or unchanged compounding ingredients. Humphrey[11] has shown that a mixture of benzene and aqueous hydrochloric acid facilitates the removal of the extraction-resistant guanidine-type accelerators. In the present work a mixture of

ethyl alcohol and 1*N* aqueous hydrochloric acid was found to be an excellent extraction medium, in that it successfully decomposes unstable accelerators and recovers the guanidine and antioxidants unchanged.

The extracted components are subsequently separated using distillation and liquid-liquid extraction techniques. The separations involved are complete, and little interference is encountered in the identification of the products.

APPARATUS

Norelco x-ray diffraction equipment was used to identify the crystalline products isolated. The photographic technique was employed, using copper K-alpha radiation.

A Beckman Model DU ultraviolet spectrophotometer was used in the identification of some of the products. Absolute ethyl alcohol was the solvent used.

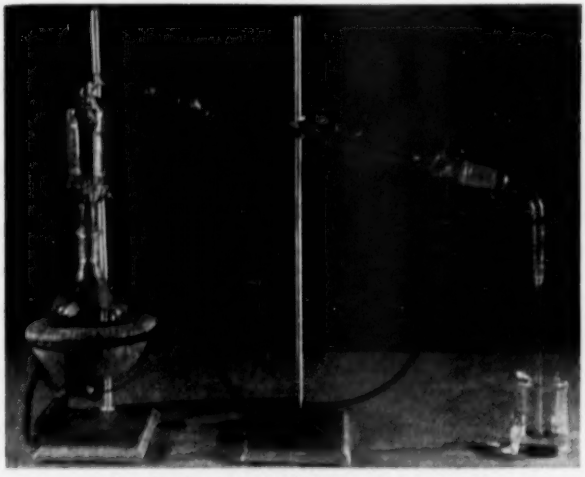


FIG. 2.—Apparatus for distilling volatile amines.

The apparatus used for extracting rubber compounds under reflux is shown in Figure 1. It consists of a 1-liter, single-necked, round-bottomed flask, fitted with a Claisen-type adapter which connects it to an air inlet tube, and to a Hopkins type reflux condenser. The upper end of the air inlet tube is connected to a gas-washing tube containing 0.5*N* alcoholic alkali to remove any traces of carbon disulfide and hydrogen sulfide from the incoming air. The lower end of this tube dips below the liquid level in the flask. Connected to the outlet tube of the reflux condenser is another gas-washing tube which contains 50 ml. of 10 per cent aqueous copper sulfate to remove any hydrogen sulfide generated during the refluxing period. A third gas-washing tube containing 0.2*N* alcoholic sodium hydroxide is used to trap the carbon disulfide that may be liberated from the rubber compound. This tube is connected to a vacuum line.

Except for gum rubber tubing connecting the gas-washing tubes, ground-glass joints are used throughout this assembly and the distillation apparatus described below.

For distillation of the amines and their absorption in acid, a conventional type of apparatus may be used, such as that illustrated in Figure 2. A modi-

fied cylindrical Kjeldahl spray trap is inserted between the distillation flask and the condenser. Modification consists of fusing an insulating jacket around the bulb, to prevent excessive liquid holdup. The receiving adapter has an outlet tip consisting of a small perforated glass bulb.

MATERIALS

All reagents and solvents used were analytical grade.

The accelerators and antioxidants used in this study were all commercial grade. They are listed in Tables I and II, with the trade names, chemical

TABLE I

ACCELERATORS STUDIED

Abbreviation or trade name	Chemical name	Source
MBT	2-Mercaptobenzothiazole	Du Pont
MBTS	2,2′-Dithiobisbenzothiazole	Naugatuck
Zenite Special	2-Mercaptobenzothiazole, zinc derivative (zinc benzothiazolyl sulfide)	Du Pont
Santocure (CBS)	*N*-cyclohexyl-2-benzothiazolesulfenamide	Monsanto
NOBS Special	2-(Morpholinothio)benzothiazole (*N*-oxydiethylene-2-benzothiazolesulfenamide)	American Cyanamid
Vulkacit AZ	*N,N*-diethyl-2-benzothiazolesulfenamide	I. G. Farbenindustrie
IBS	*N*-isopropyl-2-benzothiazolesulfenamide	Firestone[9]
CPBS	*N*-cyclopentamethylene-2-benzothiazolesulfenamide	Firestone[9]
CDETS	*N*-cyclohexyl-*S*-(diethylthiocarbamoyl)-hydrosulfamine (*N′*-cyclohexyl-*N,N*-diethylthiocarbamylsulfenamide)	Firestone[10]
Naugatuck 124	Composition not given; identified in this study as *N,N*-dicyclohexyl-2-benzothiazolesulfenamide	Naugatuck
Monex	Dimethylthiocarbamoyl sulfide (tetramethylthiuram monosulfide)	Naugatuck
Methyl Tuads	Dimethylthiocarbamoyl disulfide (tetramethylthiuram disulfide)	R. T. Vanderbilt
Ethyl Tuads	Diethylthiocarbamoyl disulfide (tetraethylthiuram disulfide)	R. T. Vanderbilt
Tetrone A	Piperidinothiocarbonyl tetrasulfide (*N,N′*-pentamethylenethiuram tetrasulfide)	Du Pont
Methyl Zimate	Zinc dimethyldithiocarbamate	R. T. Vanderbilt
Ethyl Zimate	Zinc diethyldithiocarbamate	R. T. Vanderbilt
Pipazate	Zinc *N*-pentamethylenedithiocarbamate	Naugatuck
Pip-Pip	1-Piperidinecarbodithioic acid, piperidine salt (*N*-pentamethyleneammoniumpentamethylenedithiocarbamate)	Monsanto
Philcure 113	*tert*-Butylsulfenyldimethyldithiocarbamate	Phillips Petroleum
DPG	Diphenylguanidine	Monsanto
DOTG	Di-*o*-tolylguanidine	Du Pont
TPG	Triphenylguanidine	Du Pont
Ethylac	*N,N*-diethylthiocarbamoyl-2-benzothiazolyl sulfide	Sharples
SRA No. 2	Zinc diphenylguanidinobenzothiazolylmercaptide	Du Pont

TABLE II

ANTIOXIDANTS STUDIED

Abbreviation or trade name	Chemical name	Source
AgeRite Stalite	Mixture of mono- and diheptyl-diphenylamines	R. T. Vanderbilt
BLE	Acetone-diphenylamine condensation product	Naugatuck
Flectol-H	Acetone-aniline condensation product	Monsanto
J-Z-F (DPPD)	*N,N'*-diphenyl-*p*-phenylenediamine	Naugatuck
Neozone-A	*N*-phenyl-1-naphthylamine	Du Pont
Neozone-D (PBNA)	*N*-phenyl-2-naphthylamine	Du Pont
Santoflex-AW	6-Ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	Monsanto
Santoflex-B	6-Phenyl-1,2-dihydro-2,2,4-trimethylquinoline	Monsanto
Santoflex-BX	Santoflex-B plus DPPD	Monsanto
Stabilite	*N,N'*-diphenylethylenediamine	C. P. Hall
Thermoflex	Di-*p*-methoxydiphenylamine	Du Pont
Thermoflex-A	Thermoflex plus PBNA and DPPD	Du Pont

names, and suppliers. These accelerators and antioxidants were compounded in the test formula given in Table III. *N*-Phenyl-2-naphthylamine (PBNA) was used as an antioxidant in some of the stocks compounded for accelerator identification. *N*-Cyclohexyl-2-benzothiazolesulfenamide was the accelerator used for the stocks containing different antioxidants.

PROCEDURE

The rubber vulcanizates containing the different antioxidants and accelerators listed in Tables I and II were analyzed by the procedure given below. The results of the accelerator analyses are shown in Table IV. All of the antioxidants studied were isolated in the neutral or basic fraction and successfully identified.

Extraction of Antioxidant and Accelerator Fragments from Rubber Products.—The rubber products are prepared in the usual way by mixing and sheeting out on a rubber mill. Vulcanizates can also be ground in a Wiley mill. Cements are prepared by evaporation to the solids, preferably in a vacuum oven. The solids can then be mixed and sheeted out. Compounded latex and latex products may be prepared in the same way.

TABLE III

COMPOUNDING FORMULA

Material	Parts
Natural rubber	100
Carbon black	50
Zinc oxide	3
Stearic acid	3
Paraflux (softener)[a]	4
Sulfur	2.3
Antioxidant	1 to 1.5
Accelerator[b]	0.5 to 1

All stocks, except TPG, cured 50 minutes at 280° F. TPG cured 60 minutes at 298° F.
[a] Supplied by C. P. Hall.
[b] Triphenylguanidine compounded at 1.5 parts.

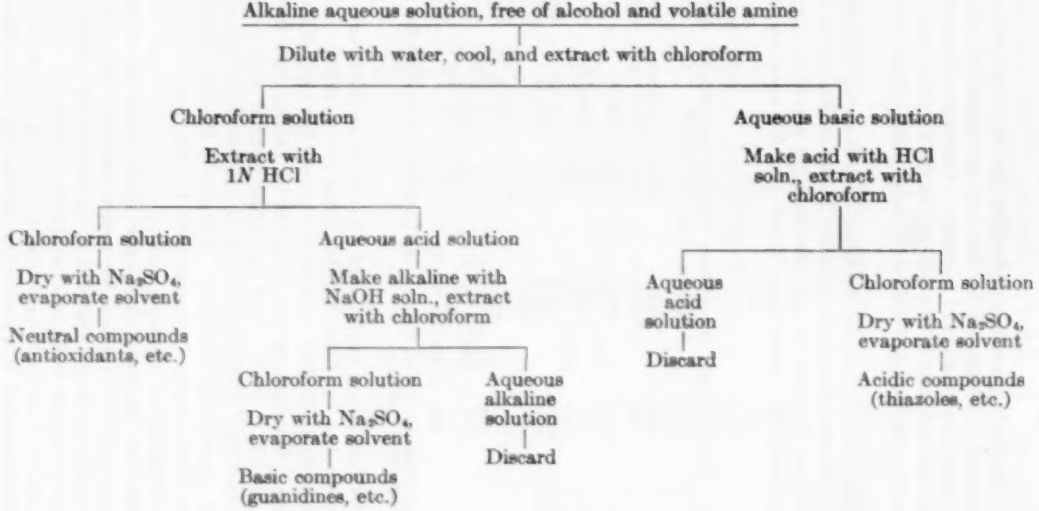
TABLE IV

RESULTS OF ACCELERATOR ANALYSES

Accelerator used	Components identified: Thiazole	Amine	Carbon disulfide	Guanidine	Accelerators indicated
Thiazolesulfenamides					
Santocure (CBS)	MBT	Cyclohexylamine	Neg.	—	Santocure
NOBS Special	MBT	Morpholine	Neg.	—	NOBS Special
Vulkacit-AZ	MBT	Diethylamine	Neg.	—	Vulkacit-AZ
Naugatuck-124	MBT	Dicyclohexylamine	Neg.	—	*N,N*-Dicyclohexyl-2-benzothiazolesulfenamide
IBS	MBT	Isopropylamine	Neg.	—	IBS
CPBS	MBT	Piperidine	Neg.	—	CPBS
Thiocarbamylsulfenamide					
CDETS	—	Cyclohexylamine + Diethylamine	Pos.	—	CDETS
Thiazoles					
MBT	MBT	—	Neg.	—	MBT, MBTS or Zenite Special
MBTS	MBT	—	Neg.	—	MBT, MBTS or Zenite Special
Zenite Special	MBT	—	Neg.	—	MBT, MBTS or Zenite Special
Thiuramsulfides and dithiocarbamates					
Monex	—	Dimethylamine	Pos.	—	Monex, Methyl Tuads, or Methyl Zimate
Methyl Tuads	—	Dimethylamine	Pos.	—	Monex, Methyl Tuads, or Methyl Zimate
Methyl Zimate	—	Dimethylamine	Pos.	—	Monex, Methyl Tuads, or Methyl Zimate
Ethyl Tuads	—	Diethylamine	Pos.	—	Ethyl Tuads or Ethyl Zimate
Ethyl Zimate	—	Diethylamine	Pos.	—	Ethyl Tuads or Ethyl Zimate
Pip-Pip	—	Piperidine	Pos.	—	Pip-Pip, Pipazate, or Tetrone A
Pipazate	—	Piperidine	Pos.	—	Pip-Pip, Pipazate, or Tetrone A
Tetrone A	—	Piperidine	Pos.	—	Pip-Pip, Pipazate, or Tetrone A
Guanidines					
DPG	—	—	Neg.	DPG	DPG or DPG salt
TPG	—	—	Neg.	TPG	TPG or TPG salt
DOTG	—	—	Neg.	DOTG	DOTG or DOTG salt
Miscellaneous					
Ethylac	MBT	Diethylamine	Neg.	—	Ethylac or Vulkacit-AZ
SRA No. 2	MBT	—	Neg.	DPG	SRA No. 2 or benzothiazole-DPG mixture
Philcure 113[a]	—	Dimethylamine	Pos.	—	*tert*-Butylsulfenyldimethyldithiocarbamate

[a] Not compounded in rubber stock, *tert*-butanethiol distilled over with amine and procedure modified to isolate and identify thiol as mercury salt.

TABLE V
SEPARATION OF NONVOLATILE, NEUTRAL, BASIC, AND ACIDIC MATERIALS


Alkaline aqueous solution, free of alcohol and volatile amine
Dilute with water, cool, and extract with chloroform
Chloroform solution
Extract with 1N HCl
Aqueous basic solution
Make acid with HCl soln., extract with chloroform
Chloroform solution
Dry with Na_2SO_4, evaporate solvent
Neutral compounds (antioxidants, etc.)
Aqueous acid solution
Make alkaline with NaOH soln., extract with chloroform
Chloroform solution
Dry with Na_2SO_4, evaporate solvent
Basic compounds (guanidines, etc.)
Aqueous alkaline solution
Discard
Aqueous acid solution
Discard
Chloroform solution
Dry with Na_2SO_4, evaporate solvent
Acidic compounds (thiazoles, etc.)

Place 15 to 20 grams of the prepared rubber product in the 1-liter, single-necked, round-bottomed flask, and add 100 ml. of ethyl alcohol and 100 ml. of 1*N* aqueous hydrochloric acid. Connect the flask to the reflux setup, and attach the gas-washing tubes. Apply enough suction to the outlet of the carbon disulfide absorption tube to permit a slow bubbling of air through all the solutions.

Turn on the heating mantle and allow the alcoholic-acid solution to reflux for approximately 2 hours. After the heat is turned off, allow air to bubble through the solutions for about 5 minutes. Disconnect the apparatus and filter the alcoholic-acid solution into a 500-ml. single-necked, round-bottomed flask. Wash the rubber residue with 100 ml. of water and add the washings to the main solution.

Distillation, recovery, and identification of amine.—Make the cooled alcoholic-acid solution alkaline with approximately 25 per cent aqueous sodium hydroxide solution, connect the flask to the distillation apparatus, turn on the heating mantle, and distill the amine into 35 ml. of 0.5*N* aqueous hydrochloric acid.

TABLE VI

ULTRAVIOLET ABSORPTION CHARACTERISTICS OF AMINE ANTIOXIDANTS AND MBT

	Min. mμ	Maxima 200–250 mμ	Min. mμ	Maxima 250–300 mμ	Min. mμ	Maxima 300–350 mμ
AgeRite Stalite	—	208(I)	253	288(II)	—	—
BJF (DPPD)	228	208(I) 240(IIIs)[a]	258	—	—	304(II)
BLE	—	208(I)	251	288(II)	—	—
Flectol-H	225	212(I) 236(II)	285	—	—	310(IIIs)
Neozone-A (PANA)	—	217(I)	236	253(II)	288	340(IIIs)
Neozone-D (PBNA)	—	220(I)	232	272(II)	283	310(III)
Santoflex-AW	—	230(I)	—	—	300	350(IIs)
Santoflex-B	—	—	—	256(I)	278	310(II)
Santoflex-BX	—	208(I)	219	256(II)	278	310(III)
Stabilite	218	212(I) 250(II)	272	294(IIIs)	—	—
Thermoflex	234	208(I) 245(IIIs)	253	288(II)	—	—
Thermoflex-A	—	220(I)	232	272(III)	282	300(II) 310(II)
MBT	234	230(II) 238(III)	—	—	272	325 (I)

For each antioxidant maxima are designated I, II, and III in descending order of intensity.
[a] s denotes slight maximum.

Continue the distillation until about 150 ml. of distillate are collected or until most of the alcohol has been distilled from the mixture. The appearance of foam in the boiling, alkaline solution indicates that the bulk of the alcohol has been distilled. Concentrate the distillate by boiling, and finally evaporate to dryness in a 110° C oven. Boil the dried residue gently with 2 or 3 ml. of chloroform and filter to separate the more soluble amine hydrochloride from the sodium and ammonium chlorides. Evaporate the chloroform at 70° C, and identify the dried amine hydrochloride by the x-ray diffraction method of Brock and Hannum[12].

Separation and identification of acid, basic, and neutral materials.—Dilute the alkaline residue from which the amine was distilled with 50 ml. of water, allow it to cool, and then subject it to an extraction procedure for separating the nonvolatile neutral, basic, and acidic materials.

The liquid-liquid extraction procedure used is similar to that employed by Braus, Middleton, and Ruchhoft[13] for separating the components of organic industrial wastes. A schematic diagram of the separation procedure is given in Table V.

The neutral fraction thus obtained normally contains the amine antioxidants, which can be identified by their ultraviolet absorption characteristics. Table VI lists the principal maxima and minima of the antioxidants included in

this study. Color tests are also helpful in identifying these antioxidants. The tests of Burchfield and Judy[14] as given below have been extremely useful.

The basic fraction will contain the guanidines, which can be identified by their x-ray diffraction diagrams. The principal diffraction maxima, together with the relative intensities of diphenylguanidine, triphenylguanidine (TPG), and di-*o*-tolyl-guanidine (DOTG), are listed in Table VII. In order to eliminate interferences due to polymorphism, all samples were recrystallized, by evaporation to dryness from chloroform, in a 110° C oven before the x-ray data were obtained.

TABLE VII
X-RAY DIFFRACTION DATA OF GUANIDINES

Diphenylguanidine (DPG)		Triphenylguanidine (TPG)		Di-o-tolylguanidine (DOTG)	
d[a]	I/I_1[b]	d	I/I_1	d	I/I_1
10.36	0.82	9.15	1.00	10.33	0.46
6.96	0.07	8.24	0.38	6.79	0.25
6.43	0.12	7.05	0.06	6.18	1.00
6.07	0.07	6.50	0.03	5.22	0.25
5.06	0.17	5.37	0.46	4.63	1.00
4.68	1.00	5.00	0.03	4.04	0.46
4.51	0.24	4.72	0.25	3.88	0.17
4.19	0.32	4.52	0.31	3.76	0.46
3.95	0.24	4.34	0.46	3.37	0.05
3.80	0.17	4.07	0.38	3.18	0.11
3.63	0.40	3.79	0.19	3.03	0.05
3.49	0.24	3.56	0.38	2.50	0.05
3.26	0.04	3.42	0.03	2.43	0.05
3.09	0.07	3.08	0.25	2.09	0.03
2.99	0.07	2.70	0.19		
2.91	0.04				
2.64	0.02				
2.54	0.04				
2.44	0.02				
2.41	0.02				
2.31	0.04				
2.21	0.04				
2.14	0.04				
2.01	0.02				
1.93	0.02				
1.86	0.04				
1.69	0.04				

[a] d. Interplanar spacing in Ångstrom units calculated from Bragg's law where $d = \frac{\lambda}{2 \sin \theta}$. λ is wave length of characteristic $CuK\alpha$ radiation, and θ is one half the angle of diffraction.
I/I_1. Relative intensity.

The acidic fraction will contain 2-mercaptobenzothiazole, if a benzothiazole-type accelerator is used. 2-Mercaptobenzothiazole is identified by its ultraviolet absorption characteristics given in Table VI. Other acidic thiazoles and related acidic materials will be isolated in this fraction. They can usually be identified by their ultraviolet absorption characteristics or x-ray diffraction diagrams.

Test for carbon disulfide.—Transfer 10 ml. of the alcoholic sodium hydroxide solution from the carbon disulfide absorption tube to a test-tube and make the solution weakly acid by the addition of glacial acetic acid. Add 5 ml. of 1 per cent aqueous copper sulfate and shake the tube thoroughly. If carbon disulfide is absent, a blue solution or a blue precipitate results. The blue precipitate will dissolve upon the addition of several drops of concentrated nitric acid. When

carbon disulfide is present, the precipitate is yellowish green, and addition of nitric acid and reshaking leave a yellow precipitate of the copper xanthate.

Color tests for antioxidants[14].—Test Solutions. Stannic Chloride Solution. Dissolve 14.7 ml. of fuming stannic chloride in anhydrous analytical reagent grade benzene and make the volume up to 250 ml.

Amyl Nitrite Solution.—Dilute 5 ml. of amyl nitrite to 100 ml. with benzene.

Test I. Stannic Chloride-Amyl Nitrite Reaction.—Dissolve approximately 1 mg. of the basic fraction in 5 ml. of benzene. Add 1 ml. of stannic chloride solution and 3 drops of amyl nitrite solution. A red precipitate indicates the presence of Stabilite.

Test II. Stannic Chloride-Benzotrichloride Reaction.—Dissolve approximately 1 mg. of the neutral fraction in 5 ml. of pure ethylene dichloride. Add 1 ml. of stannic chloride solution and 2 drops of benzotrichloride. BLE (an acetone-diphenylamine condensation product) gives a violet color with this test, differentiating it from AgeRite Stalite (a mixture of mono- and dihepthyldiphenylamines), which gives an insignificant yellow color.

INTERPRETATION OF RESULTS

The accelerators used in the rubber product are determined by the fragments or combination of fragments identified. A knowledge of normal compounding practices will aid in reconstructing the accelerator system used. In general, the detection of a thiazole, a guanidine, or carbon disulfide will classify the accelerator as to type—namely, a thiazole, usually 2-mercaptobenzothiazole or a derivative, a guanidine, or a thiuramsulfide or dithiocarbamate. The specific amine identified, if any, designates the particular amine activator, sulfenamide, thiuram sulfide, or dithiocarbamate used. Table IV lists the accelerators, which are indicated by the components identified.

Although the antioxidant is usually identified by its ultraviolet absorption characteristics, some antioxidants are indicated by color reactions inherent in the procedure. Antioxidants containing *N,N'*-diphenyl-*p*-phenylenediamine (DPPD) and di-*p*-methoxydiphenylamine (Thermoflex) are indicated by a green or blue-green color in the cooled extraction medium. When Thermoflex is present, the color turns red as the extraction medium is made alkaline with sodium hydroxide. If DPPD is present, the alkaline solution is a yellow-brown color. Other color tests are used to distinguish between antioxidants having similar ultraviolet absorption characteristics. Consequently BLE can be distinguished from AgeRite Stalite by color test II (stannic chloride-benzotrichloride reaction).

N,N'-Diphenylethylenediamine (Stabilite) is the only one of the antioxidants studied which was recovered in the basic fraction. Stabilite can be identified in the presence of the guanidines by color test I (stannic chloride-amyl nitrite reaction).

The xanthate test was found to give a good positive test for carbon disulfide in the case of thiuram and dithiocarbamate type accelerators, and a negative test with other accelerators. If a more sensitive test is used, accelerators other than thiurams and dithiocarbamates may give a slight positive test for carbon disulfide and confuse the identification.

DISCUSSION

One disadvantage of this procedure is that some accelerators give identical decomposition products. As a result, it is impossible to differentiate between

2-mercaptobenzothiazole, 2,2′-dithiobisbenzothiazole, and 2-mercaptobenzothiazole, zinc derivative (Zenite Special). Similarly, no distinction can be made between thiuram sulfides and dithiocarbamates containing the same amine. This disadvantage is minimized in view of the fact that these accelerators undergo interconversion or decomposition during vulcanization, and identification of the original accelerator is always difficult.

The identification of accelerators and antioxidants in aged vulcanizates introduces the problem of decomposition due to aging. Burchfield and Judy[14] have recognized this difficulty in the identification of antioxidants. No detailed study of aged samples was made in the present investigation. It was observed, however, that 2-(morpholinothio)benzothiazole (NOBS Special) could not be identified in aged stocks and was difficult to identify in freshly cured vulcanizates. Santocure and DPG, on the other hand, could be identified easily in vulcanizates aged as long as three years. Antioxidants isolated from aged stocks gave ultraviolet absorption characteristics which were generally more difficult to identify.

Mixtures of antioxidants, as would be expected, are more difficult to identify, but they can usually be resolved by careful examination of the ultraviolet absorption data and by using color tests. Mixtures of accelerators generally do not present too much of a problem, since their decomposition products usually occur in different fractions.

To demonstrate the usefulness of the method in identifying mixed accelerators and antioxidants, a vulcanizate was prepared containing Santocure, Ethyl Tuads, TPG, BLE, and Santoflex BX (a mixture of 6-phenyl-1,2-dihydro-2,-2,4-trimethylquinoline and DPPD). All five of the isolated fractions contained at least one product. The identification of cyclohexylamine and MBT indicated the presence of Santocure. Diethylamine and carbon disulfide indicated the use of Ethyl Tuads or zinc diethyldithiocarbamate (Ethyl Zimate). TPG was identified in the basic fraction. BLE, DPPD, and 6-phenyl-1,2-dihydro-2,2,4-trimethylquinoline (Santoflex B) were all indicated to be present in the neutral fraction. As Santoflex B and DPPD partially obscure the ultraviolet absorption characteristics of BLE, the presence of the latter is confirmed by color test II.

The extracted portion of the softeners used in compounding will usually be isolated in the neutral fraction. If these materials exhibit characteristic ultraviolet absorption, they could possibly interfere with the identification of the antioxidants. However, in the present study, no undue interference was encountered from either Paraflux or pine tar. This is primarily due to the fact that the aqueous alcohol extraction medium has little solvent power on softeners that are insoluble in water.

The presence of large amounts of oils, in oil-extended polymers, interferes seriously with the identification of antixoidants. In such cases it may be necessary to resort to chromatographic techniques before satisfactory results can be obtained.

APPLICATIONS

The procedure described here is offered as a new approach to the determination of accelerators and antioxidants in rubber products. It has been applied successfully to both vulcanized and unvulcanized rubber compounds. It is equally useful in the analysis of latex products and rubber cements. Data on 24 accelerators and 12 antioxidants have been obtained in this study.

The method has been used also in the identification of new accelerators.

The analytical scheme is such that it will include many of the accelerators which are likely to be developed in the near future—for example, the recently reported accelerator, *tert*-butylsulfenyldimethyl dithiocarbamate (Philcure-113)[15], has been identified by the method. The procedure was modified slightly to include the identification of the thiol portion of the molecule (see Table IV).

The method will also have use in identifying some of the newer combinations of accelerators, such as the combination of the thiuram and guanidine types which has been recommended for use in the vulcanization of Neoprene Type W[16].

SUMMARY

A new, simple, and comprehensive approach to the identification of the accelerators and antioxidants used in rubber products is described. This procedure is unusual in that it utilizes the tendency of accelerators to decompose during mixing or vulcanization, or on extraction from compounded stocks. The accelerator fragments are isolated using distillation and liquid-liquid extraction principles. The identification of the fragments is simple, rapid, and unambiguous. The accelerators used are then determined from a knowledge of the decomposition behavior of known compounds. The antioxidants are recovered unchanged and can be identified by their ultraviolet absorption characteristics and color tests. This method is applicable to all types of rubber products, including cements, and is particularly valuable in the identification of accelerators which decompose on mixing, vulcanization, or extraction. Most of the commonly used accelerators and amine antioxidants can be classified or identified by the analytical scheme described. The procedure will be useful in identifying many accelerators and antioxdiants which may be developed in the future.

ACKNOWLEDGMENT

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COLORIMETRIC DETERMINATION OF PHENYL-2-NAPHTHYLAMINE IN RUBBER *

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For identifying antioxidants in rubber, several types of color reactions are mentioned in the literature[1]. Burchfield and Judy[2] classify these reactions in six groups as follows:

1. Reaction of $SnCl_4$ and amyl nitrite.
2. Reaction of $SnCl_4$ and trichlorobenzene.
3. Coupling reaction of the antioxidant with diazotized *p*-nitroaniline.
4. Oxidation by benzoyl peroxide.
5. Reaction of indamine.
6. Reaction of $SnCl_4$ and bromine.

The authors have arranged these reactions in a chart which shows readily how they can be used for the identification of several current antioxidants.

Further a work of Deal[3] should be brought to attention, which mentions five new types of color reactions of antioxidants with nitric and sulfuric acid and with sulfuric acid with the additions of ammonium persulfate, molybdenum trioxide, and selenium dioxide.

A study of these color reactions was a stimulus to us to work out quantitative colorimetric procedures. The most suitable color reaction for the phenyl-2-naphthylamine was with diazotized *p*-nitroaniline. A water solution of this substance, if added to an acetone solution of phenyl-2-naphthylamine, produced an intense red color. The intensity of the coloration increases gradually on evaporation of the acetone, and it is therefore recommended to take the photometric measurement immediately after the addition of the coupling agent to the sample. The presence of compounds with amino groups (for example, accelerators) interferes with the determination.

SOLUTIONS EMPLOYED

1. *Coupling agent.*—1 g. of *p*-nitraniline was dissolved in a mixture of 25 ml. concd. hydrochloric acid and 25 ml. water, and the volume was repleted with water to 100 ml. For the preparation of diazotized *p*-nitroaniline, 25 ml. of this solution was pipeted out, 5 ml. of 2.5% solution of sodium nitrite was added to it, and the mixture was left 15 minutes to react.

2. *Standard solutions of amine.*—0.1 to 2.0 mg. of phenyl-2-naphthylamine was dissolved in acetone and the volume made up to 100 ml.

EXPERIMENTAL PART

0.7 mg. of phenyl-2-naphthylamine was dissolved in acetone and the volume repleted to 100 ml. After the addition of 1 ml. of the coupling agent, the dependence of extinction on the wave length of the light employed was measured.

* Translated for Rubber Chemistry and Technology by Louis A. Helwich from *Chemický Průmysl*, Vol. 5(30), No. 5, pages 212–213, May 1955.

Screen no.	Extinction	Screen denomination	Wave length mμ
1	0.020	S 75	750
2	0.038	S 72	720
3	0.061	S 66	660
4	0.085	S 61	610
5	0.342	S 57	570
6	0.700	S 53	530
7	0.601	S 50	500
8	0.444	S 47	470
9	0.722	S 42	420

mg. amine in 100 ml.	Extinction
0.1	0.103
0.2	0.202
0.4	0.401
0.6	0.585
0.8	0.793
1.0	0.992
1.2	1.201
1.4	1.402
1.6	1.613
1.8	1.805
2.0	2.000

As can be seen from the curve in Figure 1, the maximum extinction found was around 530 mμ.

To prove the validity of the Lambert-Beer law, standard samples were prepared by dissolving 0.1 to 2.0 mg. of phenyl-2-naphthylamine in 100 ml. acetone. To these solutions was added 1 ml. of diazotized *p*-nitroaniline (1 ml. of coupling agent for 100 ml. of acetone solution of phenyl-2-naphthylamine) and the measurement was made immediately. The intensity of the coloration developed was measured by a Pulfrich photometer, using a light-green screen No. 6, passing the light of wave length 530 mμ (extinction maximum—see Figure 1), in a cuvette of 10 mm. side-length, which allowed the measuring to be made above and also below the concentration of 1.0 mg. of phenyl-2-naphthyl-

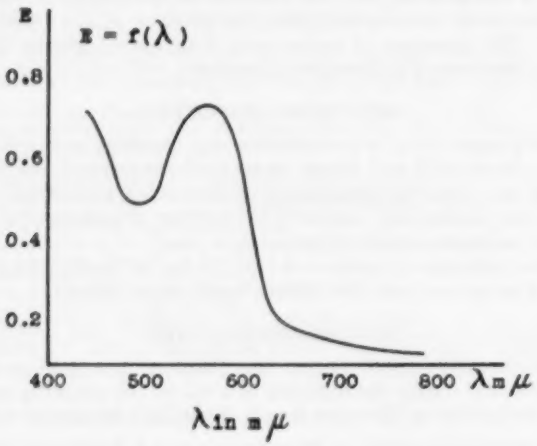

Fig. 1.

amine in 100 ml. of acetone. The resulting extinction was taken as a mean value of 10 measurements.

A curve was obtained which shows the linear dependence of extinction on the concentration of phenyl-2-naphthylamine, in the range between 0.1 and 2.0 mg. in 100 ml. of the solution (see Figure 2). The extinction, measured

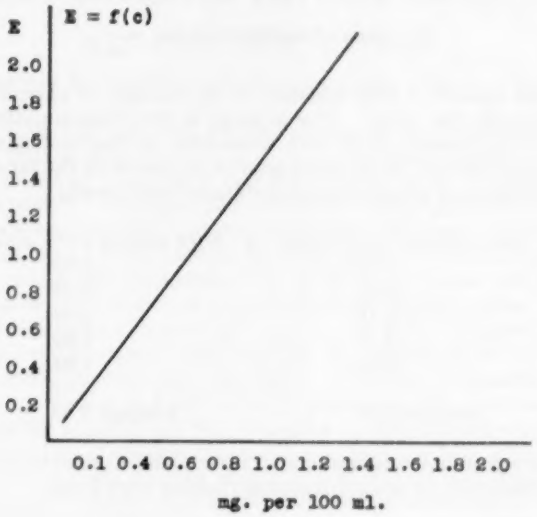

FIG. 2.

under the given conditions, gives directly the mg. of phenyl-2-naphthylamine (that is, the molar coefficient K is equal to 1).

In measuring the extinction of the prepared sample, it was found that the intensity of coloration in open cuvettes gradually increases with time.

Thus the extinction of the solution was:

Measured immediately	1.14
After standing one hour	1.18
After standing two hours	1.24

PROCEDURE FOR COPOLYMERS

The determination of phenyl-2-naphthylamine in copolymers is made as follows. Approximately 1 g. of weighed sample of Buna is extracted by acetone for 3 hours. After the phenyl-2-naphthylamine has been removed by extraction, the apparatus is rinsed by acetone, and the volume of the united extracts, after cooling to room temperature, is made up with acetone to 100 ml. From this solution an amount of sample is pipetted out, which, after making up its volume with acetone to 100 ml. and adding 1 ml. of coupling agent, would produce an intensity of coloration lying within the limits of validity of the Lambert-Beer law. From the extinction found, which gives directly the number of milligrams of phenyl-2-naphthylamine in 100 ml. of the acetone solution, the percentage sought is then computed.

COMPUTATION

Weighed amount of copolymer a g., acetone extract made up to 100 ml., 10 ml. pipetted-out and again the volume made to 100 ml. The extinction found gives b mg. of phenyl-2-naphthylamine in the original pipetted 10 ml.

The whole acetone extract therefore contains 10 b mg. of phenyl-2-naphthylamine.

$$\% \text{ phenyl-2-naphthylamine} = \frac{b}{a}$$

To test the method, a determination of the amount of phenyl-2-naphthylamine in Buna-SS was made. The average of five determinations was 1.68 per cent. New determinations were made after adding and mixing 0.5 and 1.0 per cent, respectively, of phenyl-2-naphthylamine with the same samples.

The percentages of phenyl-2-naphthylamine found were:

1. After adding 0.5% amine	2. After adding 1.0% amine
2.15	2.62
2.15	2.63
2.16	2.64
2.15	2.62
2.14	2.64
Average 2.15	Average 2.63

As an average of 5 determinations in these artificial samples, 2.15 and 2.63 per cent, respectively, of phenyl-2-naphthylamine were found.

SUMMARY

A colorimetric method was worked out for the determination of the amount of phenyl-2-naphthylamine in butadiene-styrene copolymers based on the coupling reaction of phenyl-2-naphthylamine with diazotized *p*-nitroaniline. The method was found practically applicable. It is accurate, and the procedure is simple.

REFERENCES

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[2] Burchfield and Judy, *Anal. Chem.* **19**, 786 (1947).
[3] Deal, *Trans. Inst. Rubber Ind.* **23**, 148 (1947).

VOLATILE ACIDS AND THE QUALITY OF CONCENTRATED NATURAL LATEX *

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Much attention has been paid to the variation in the properties of natural rubber latex[1], and important among the causes of variation are the acidic products of decomposition, which have considerable effects on conductivity[1] and mechanical stability[2]. The importance of acidic components on the chemical stability of latex compounded with zinc oxide has also been well discussed[3].

Until recently the acidic content of latex has usually been determined by the KOH no. test, which estimates most of the acidic ions in latex, but has the disadvantage that no differentiation is made between the long-chain stabilizing acids and the short-chain destabilizing ones[4]. In 1953, Philpott and Sekar[5] showed that the short-chain volatile fat acids can be determined by steam distillation of serum from acid-coagulated latex. They have indicated that volatile acids develop rapidly in fresh and lightly ammoniated latex and that the presence of volatile acids affects the properties of concentrated latex.

The determination of volatile fat acids has been found to be a useful method for controlling the quality of latex concentrate in commercial production. In this paper, effects of volatile acids on the properties of ammoniated centrifuged concentrate and factors affecting the development of volatile acids are discussed.

EXPERIMENTAL

The determinations of dry rubber content, total solids, ammonia and KOH no. were carried out using the methods recommended by the American Society for Testing Materials[6]. Mechanical stability was determined at a dilution of 51.5 per cent total solids, using the 1951 ASTM method[7] and the Klaxon stability apparatus[8].

Specific conductivity was measured at 30° C, using a Cambridge conductivity bridge, which is based on the Wheatstone bridge principle.

The method employed for volatile fat acid number (VFA no.) was a simplification of the macro-scale, constant volume method described by Philpott and Sekar[5]. For 118 estimations, a marked relationship was found to exist between the titer value of the first 50 ml. of distillate (x), using 0.01 N sodium hydroxide and the calculated titer value for the total volatile fat acids in 50 grams of latex (y). The regression equation was $y = 1.43 + 9.18x$. About half an hour was required for this simplified method, compared with about two hours for the full determination. Details of the method used are as follows.

Weigh 50 g. of latex of known total-solids content. Add 100 ml. of distilled water, then slowly add 20 ml. of 5 N sulfuric acid mixed with 5 ml. of distilled water to coagulate the latex. Filter the serum through a Buchner funnel. Pipette 100 ml. of clear serum into the distilling flask and add 50 ml. of distilled water. Add a drop of antifoaming agent (Siotol-AF). Steam distill at con-

* Reprinted from the *Journal of the Rubber Research Institute of Malaya*, Vol. 14, pages 407–422, December 1955.

TABLE I

PREPARATION OF CENTRIFUGED CONCENTRATE WITH INCREASING VFA NO.

Age of field latex when centrifuged	Field latex: VFA no.	Field latex: NH_3 (%wt.)	Concentrate (tested on the day of centrifuging): Total solids (%wt.)	Concentrate: NH_3 (%wt.)	Concentrate: VFA no.	Concentrate: KOH no.	Concentrate: Specific conductivity (mhos $\times 10^6$)	Concentrate: Mechanical stability (seconds)
1. Latex from clone Tjir 1 (41.66% total solids)								
(a) 6 hours	0.03	0.33	60.46	0.72	0.02	0.34	3.55	65
(b) 5 days	0.35	0.26	59.23	0.78	0.21	0.71	4.87	68
(c) 11 days	0.88	0.36*	57.43	1.08	0.53	1.24	6.87	53
2. Mixed clonal and seedling latex (42.32% total solids)								
(a) 6 hours	0.03	0.40	60.11	0.83	0.02	0.37	3.27	63
(b) 3 days	0.18	0.36	62.12	0.76	0.12	0.52	3.89	59
(c) 4 days	0.41	0.34	59.55	0.76	0.25	0.75	4.82	56
(d) 10 days	1.01	0.29	57.64	0.96	0.50	1.10	6.55	89

* Ammonia increased after 10 days before centrifuging.

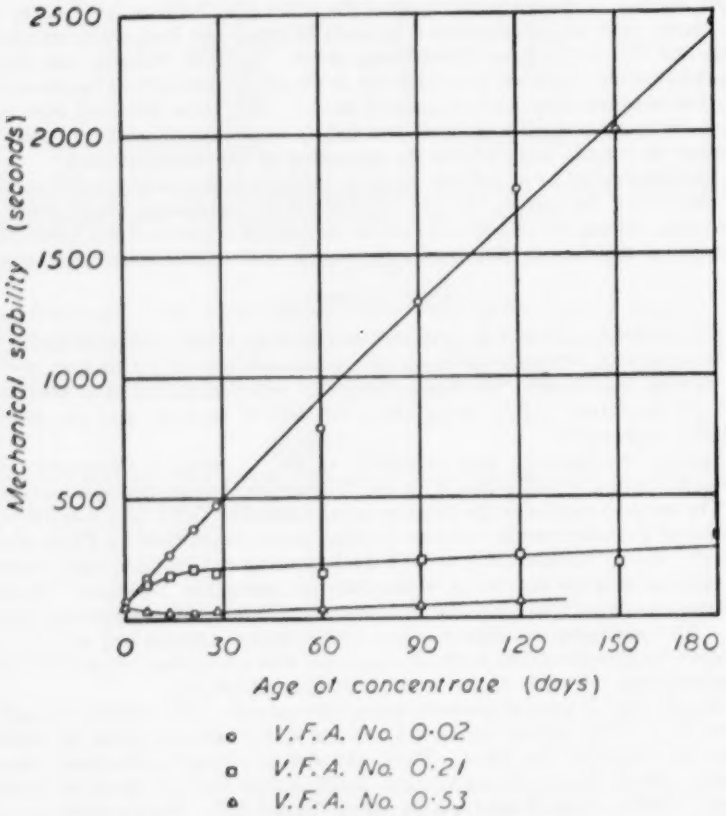

FIG. 1.—Increase of mechanical stability on storage of concentrates made from Tjir 1 latex at three levels of VFA no.

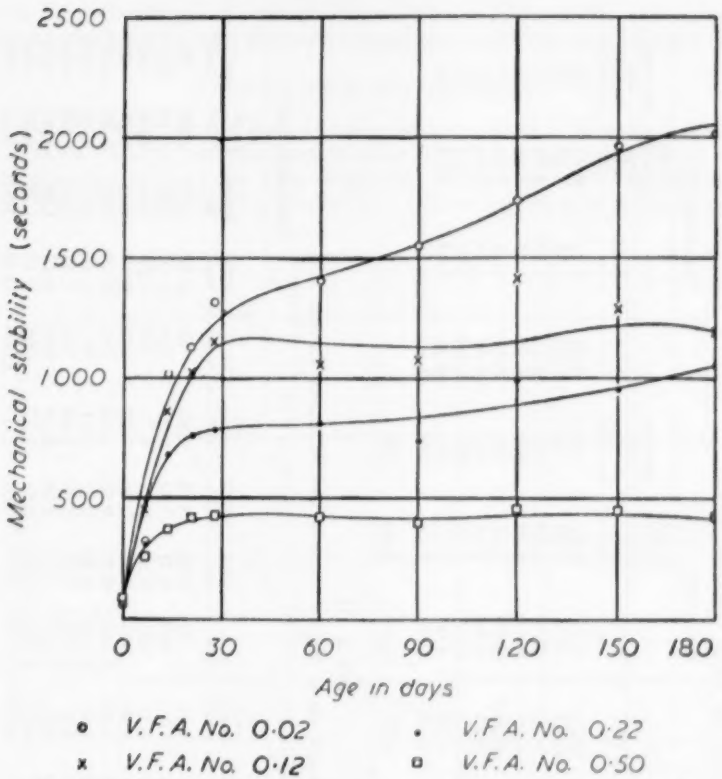

FIG. 2.—Increase of mechanical stability on storage of concentrates made from mixed clonal and seedling latex at four levels of VFA no.

stant volume and collect 50 ml. of distillate in 15 minutes. Titrate the distillate with 0.01*N* sodium hydroxide, using phenolphthalein as indicator.

Determine a blank titration of 50 ml. of distillate from 20 ml. of 5*N* sulfuric acid and 130 ml. of distilled water with a drop of antifoaming agent.

CALCULATION

Subtract the blank titer value from the serum distillate titer value to give a corrected titer value (x). Calculate the titer value (y) of volatile acids in 50 g. of latex from the equation:

$$y = 1.43 + 9.18\,x$$

The VFA no. is usually reported as g. of potassium hydroxide per 100 g. total solids. Therefore:

$$\text{VFA no.} = \frac{y \times 0.000561 \times 100 \times 2}{\%\ \text{total solids}}$$

$$= \frac{0.1122 \times y}{\%\ \text{total solids}}$$

TABLE II

STORAGE OF TJIR 1 CONCENTRATE

Age of concentrate when tested (days)	Concentrate 1 (a)				Concentrate 1 (b)				Concentrate 1 (c)			
	VFA no.	KOH no.	Specific conductivity (mhos $\times 10^9$)	Mechanical stability (seconds)	VFA no.	KOH no.	Specific conductivity (mhos $\times 10^9$)	Mechanical stability (seconds)	VFA no.	KOH no.	Specific conductivity (mhos $\times 10^9$)	Mechanical stability (seconds)
0	0.02	0.34	3.55	65	0.21	0.71	4.87	68	0.53	1.24	6.87	53
7	0.02	0.46	3.84	171	0.22	0.74	5.27	138	0.56	1.28	6.87	33
14	0.04	0.50	3.81	260	0.22	0.79	4.92	175	0.51	1.30	6.76	27
21	0.03	0.51	3.92	371	0.21	0.84	5.22	202	0.46	1.33	6.40	29
28	0.03	0.56	3.74	473	0.20	0.88	5.41	188	0.56	1.49	7.04	30
60	0.04	0.56	3.71	785	0.22	0.94	5.55	187	0.52	1.38	7.16	36
90	0.03	0.62	4.07	1,309	0.20	0.94	5.78	228	0.50	1.39	7.54	50
120	0.04	0.64	4.76	1,770	0.20	1.00	5.51	253	0.48	1.52	6.72	66
150	0.04	0.66	4.71	2,018	0.18	0.98	5.94	225	Latex flocculated			
180	0.04	0.72	4.46	2,453	0.23	1.04	6.08	332				

TABLE III

STORAGE OF CONCENTRATE FROM MIXED CLONAL AND SEEDLING LATEX

Age of concentrate when tested (days)	Concentrate 2 (a)				Concentrate 2 (b)				Concentrate 2 (c)				Concentrate 2 (d)			
	VFA no.	KOH no.	Sp. cond. (mhos $\times 10^9$)	M. s. (sec)	VFA no.	KOH no.	Sp. cond. (mhos $\times 10^9$)	M. s. (sec)	VFA no.	KOH no.	Sp. cond. (mhos $\times 10^9$)	M. s. (sec)	VFA no.	KOH no.	Sp. cond. (mhos $\times 10^9$)	M. s. (sec)
0	0.02	0.37	3.27	63	0.12	0.52	3.89	59	0.25	0.75	4.82	56	0.50	1.10	6.55	89
7	0.02	0.46	3.53	328	0.11	0.64	4.07	462	0.21	0.84	4.97	318	0.50	1.23	6.12	271
14	0.03	0.51	3.65	1,015	0.12	0.64	4.03	863	0.23	0.81	4.71	685	0.50	1.15	6.65	382
21	0.03	0.50	3.34	1,125	0.13	0.64	4.28	1,025	0.23	0.80	5.24	766	0.49	1.12	6.35	424
28	0.04	0.51	3.62	1,316	0.12	0.62	3.88	1,156	0.22	0.80	4.94	791	0.49	1.15	6.88	437
60	0.02	0.52	3.81	1,403	0.11	0.62	4.40	1,051	0.20	0.81	5.41	811	0.46	1.17	6.35	429
90	0.03	0.56	4.10	1,549	0.12	0.69	4.51	1,076	0.21	0.93	5.49	744	0.47	1.26	7.03	409
120	0.02	0.57	4.22	1,737	0.10	0.69	4.66	1,417	0.22	0.88	5.69	992	0.45	1.28	6.81	463
150	0.02	0.65	4.28	1,964	0.12	0.82	4.67	1,295	0.23	0.97	5.37	956	0.46	1.28	6.67	454
180	0.03	0.71	4.21	2,016	0.12	0.76	4.63	1,194	0.24	0.93	5.37	1,058	0.48	1.31	6.55	433

Sp. cond. = Specific conductivity.
M.s. = Mechanical stability.

All determinations and observations were made in duplicate, and each experiment was repeated on a separate bulk of latex collected on a different day.

VOLATILE ACIDS AND STABILITY

Field latex was collected from two sources at the Rubber Research Institute Experiment Station, namely, latex of clone Tjir 1 and old mixed clonal and seedling latex. The latexes were ammoniated to 0.3 per cent NH_3 and four gallon lots were centrifuged immediately. Other samples were retained until

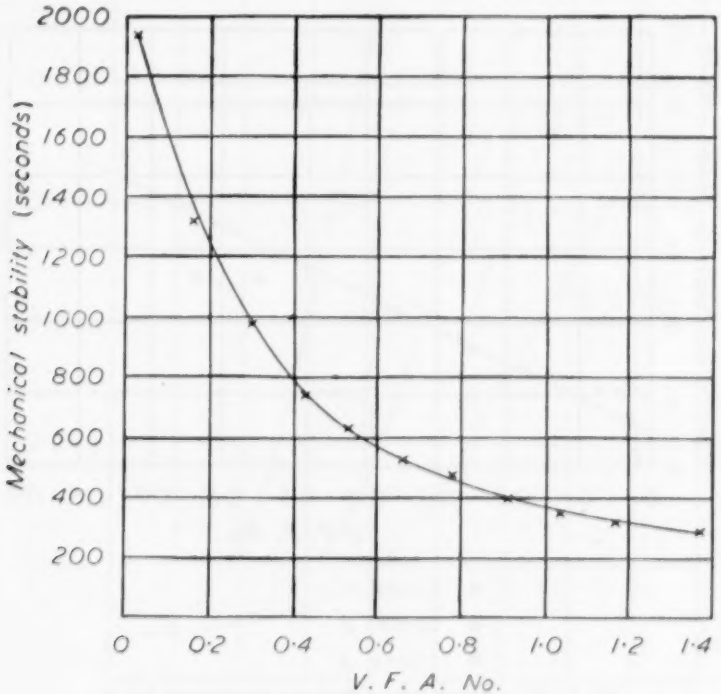

FIG. 3.—Effect of addition of ammonium acetate on the mechanical stability of a well preserved concentrate.

the VFA no. had reached values of about 0.2, 0.4, 0.8 and 1.0 before centrifuging. Concentrates were immediately ammoniated to over 0.7 per cent NH_3. Data on the development of volatile acids and initial tests on the concentrates are given in Table I.

Samples of the concentrates were stored in winchester quart bottles and tested after 7, 14, 21, 28, 60, 90, 120, 150, and 180 days. Storage effects on mechanical stability are shown in Figures 1 and 2 and changes in other properties are given in Tables II and III.

The main effect of the presence of volatile acids on mechanical stability was the prevention of increase on storage. This was very marked with the Tjir 1 concentrate when with a VFA no. of 0.02 the mechanical stability reached a

value of over 2000 seconds after six months, whereas with a VFA no. of 0.21 the mechanical stability remained constant after three weeks at values about 300 seconds.

Philpott and Sekar[5] state that the volatile acids consist mainly of acetic acid, which is present in the latex serum as ammonium acetate. They have shown that mechanical stability was depressed by the addition of ammonium acetate. The effects of adding varying amounts of a 20 per cent solution of ammonium acetate to six months old concentrate (see Tables I and III 2(*a*)) are shown in Figure 3.

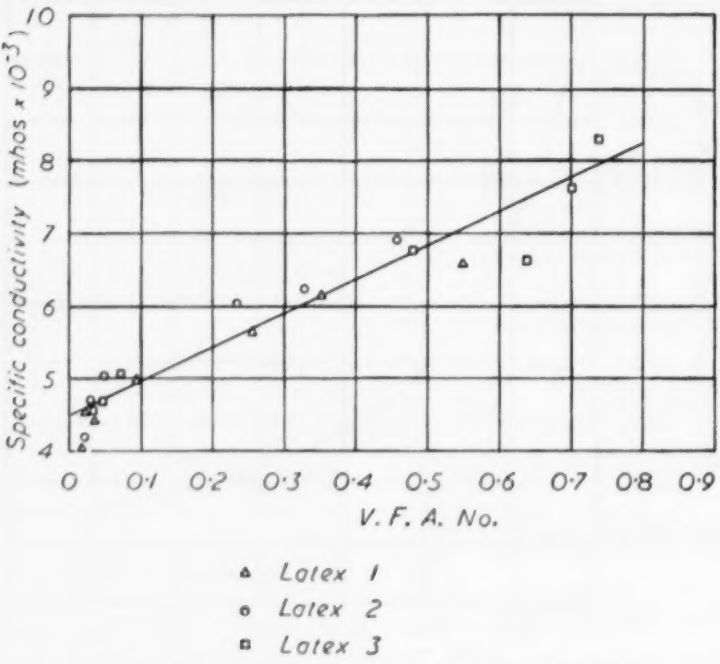

FIG. 4.—The correlation between electrical conductivity and VFA no.

The increase of the mechanical stability on storage is usually attributed to the slow formation of long chain fat acid ammonium soaps, which probably account in part for the slow increase in KOH no. on storage. When a latex has a high VFA content at the outset the slow formation of the long chain acid soaps still occurs (see Tables II and III), but their normal effect on the mechanical stability is negatived by the presence of the VFA anions. It is suggested that this depressant effect on stability is the result of the increase in ionic strength which accompanies high VFA content (see Table I). This increased ionic strength results in increased electrical conductivity, but a high conductivity in a given latex is not solely caused by a high VFA content because the conductivity of a fully preserved latex increases on storage, even when the VFA remains unaltered.

VOLATILE ACIDS AND CONDUCTIVITY

Stamberger[9] has suggested that the rate of degradation in latex can be traced by conductivity determinations, and Murphy[10] and Paton[11] have shown that specific conductivity has a linear relationship with KOH no. It will be seen from tables II and III that specific conductivity increases both with the VFA no. and the KOH no. of latex concentrate. Madge[12] suggests that long-chain

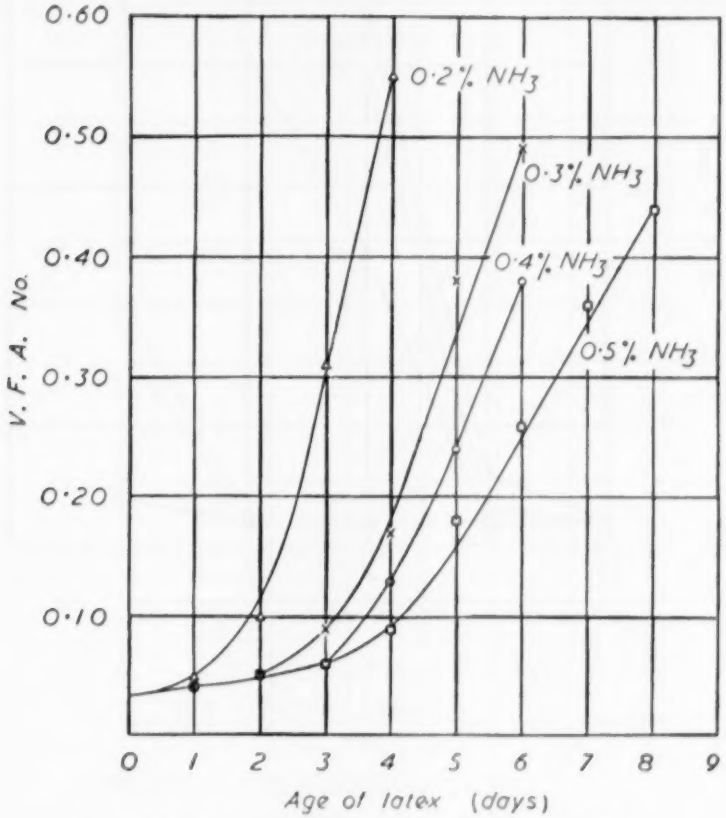

FIG. 5.—Effect of different levels of ammoniation on the increase in VFA no.

ammonium soaps contribute more to the KOH no. than to conductivity, and it seems likely therefore that there may be a direct relationship between VFA no. and conductivity in freshly ammoniated field latex, where the long chain soaps have not usually been formed to any great extent.

Three latexes from different sources were ammoniated to about 0.35 per cent NH_3 and stored in stoppered demijohn bottles and in loosely covered buckets. Specific conductivities and VFA nos. were determined at approximately the same time each day for a week and the results are plotted in Figure 4. Statistical examination indicates a significant linear relationship between specific

conductivity $\times 10^3$ (y) and VFA no. (x) and a regression equation for the data is $y = 4.50 + 4.7x$. However, an insufficient number of latexes have been examined to justify adoption of this equation as a general rule. In practice, a field latex conductivity exceeding 5×10^{-3} mhos indicates a VFA no. above 0.1.

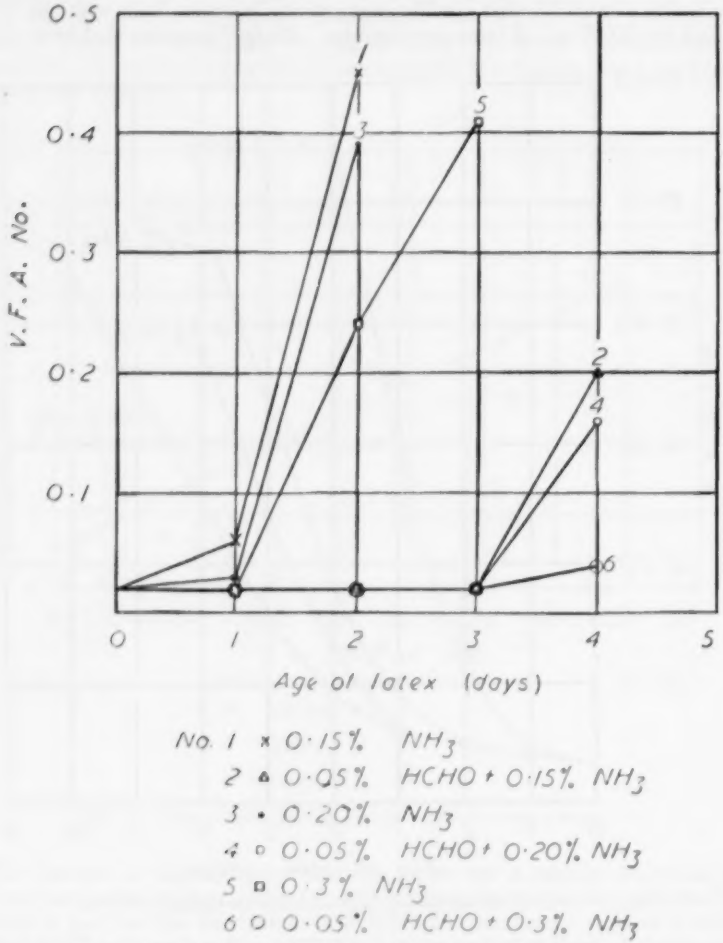

FIG. 6.—Addition of formaldehyde delays the rise of VFA no. for several days.

The measurement of specific conductivity is quicker than the usual method for determining volatile acids, and might prove to be a useful method for factory control when many bulks of field latex have to be rapidly tested for quality.

DEVELOPMENT OF VOLATILE ACIDS

Since the formation of volatile acids in latex is mainly due to the action of micro-organisms[5], the quality of concentrate should depend largely on inhibition

of contaminating bacteria by adequate preservation of the field latex. The following factors have been investigated:

Ammonia content.—Four gallon samples of mixed seedling and clonal latex were ammoniated to 0.2, 0.3, 0.4 and 0.5 per cent NH_3 and stored in buckets with loose covers. VFA nos. were determined each afternoon until values of about 0.5 were reached. The development of volatile acids with age of the

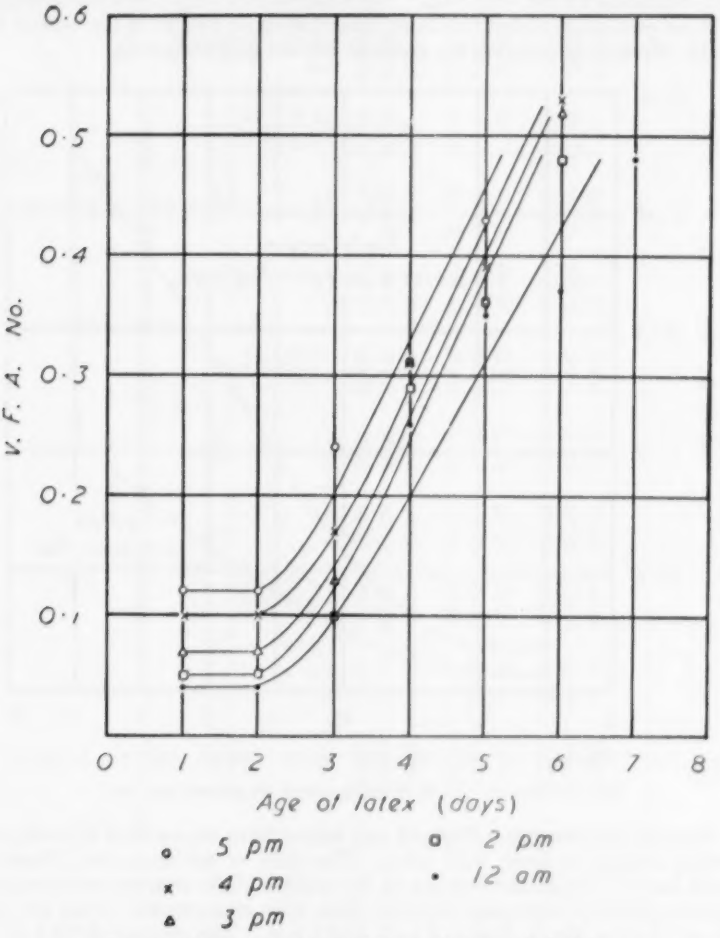

FIG. 7.—Effect of delay in ammoniation on the increase in VFA no.

latex is shown in Figure 5. The curves show that the formation of volatile acids is delayed for a certain time, depending on the amount of ammonia present, thereafter they increase rapidly, and this rapid increase usually takes place after a value of 0.1 is reached.

Use of formaldehyde.—Similar samples of latex to the above were treated with 0.05 per cent formaldehyde one hour before ammoniating to 0.15, 0.2 and

0.3 per cent NH_3. The development of volatile acids is compared in Figure 6 with development in latex containing 0.3 per cent NH_3 only. The addition of formaldehyde delayed the production of volatile acids for longer periods than did comparable quantities of ammonia alone. Centrifuged concentrate prepared from three-days-old field latex treated with formaldehyde and ammonia compared favorably in properties with concentrate prepared from fresh field latex containing 0.3 per cent NH_3. The addition of 0.05 per cent formaldehyde to 0.3 per cent ammoniated field latex immediately on receipt at the factory was equally effective in delaying the onset of volatile acid formation.

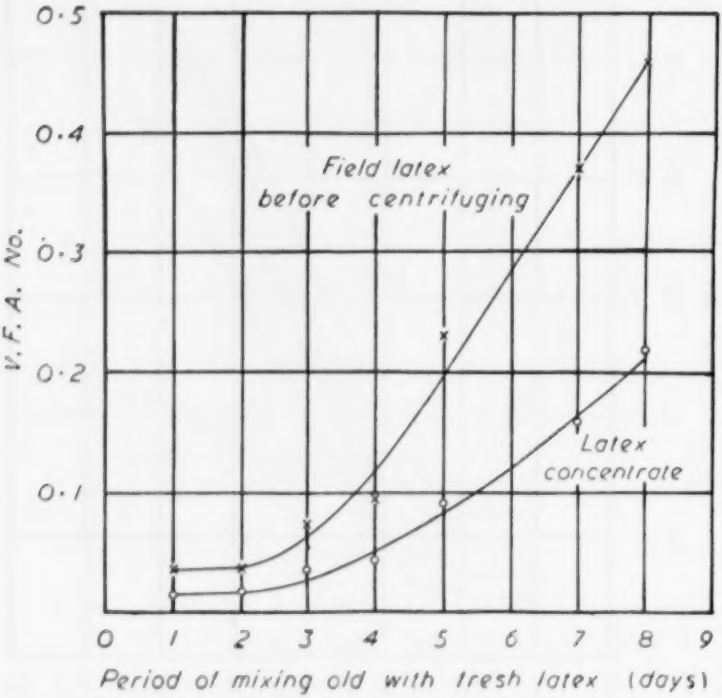

FIG. 8.—Effect on VFA no. of adding some of the previous days' crop.

Time of ammoniation.—Philpott and Sekar[8] have shown that volatile acids develop rapidly in fresh field latex. The time of ammoniation, therefore, should have an important bearing on the quality of the concentrate produced. Samples of mixed clonal and seedling latex were ammoniated to 0.3 per cent NH_3 at 12 noon, 2 p.m., 3 p.m., 4 p.m., and 5 p.m. The increase of VFA no. on storage is shown in Figure 7. Delay in ammoniating caused an increase in the VFA no. of the field latex, which would be reflected in a higher VFA no. in the concentrate.

Mixing old and new field latex.—It is sometimes a practice in latex factories not to centrifuge all of each day's latex within twenty four hours of collection, but to mix freshly collected latex with some of the old material. To find the effect of this practice on the VFA no. of concentrate, 90 gallons of mixed seedling

TABLE IV

RELATION BETWEEN VFA NO. OF FIELD LATEX, CONCENTRATE AND SKIM

Type of latex	Field latex			Concentrate			Skim			Volatile acids expressed as g. KOH per 100 g. serum (i.e., 100-d.r.c.)		
	t.s. (%wt.)	d.r.c. (%wt.)	VFA no. (g. KOH 100 g. t.s.)	t.s. (%wt.)	d.r.c. (%wt.)	VFA no. (g. KOH 100 g. t.s.)	t.s. (%wt.)	d.r.c. (%wt.)	VFA no. (g. KOH 100 g. t.s.)	Field latex	Concentrate	Skim
Mixed clonal and seedling latex	**39.82**	**36.38**	**0.056**	**57.82**	**55.62**	**0.025**	**14.11**	**9.14**	**0.142**	**0.035**	**0.033**	**0.022**
from RRI Expt. Station	39.82	36.38	0.341	64.30	62.41	0.121	15.56	10.12	0.736	0.213	0.207	0.128
	39.82	36.38	0.535	57.54	54.62	0.300	15.63	9.76	1.89	0.335	0.380	0.328
Mixed seedling latex from Ulu	37.05	34.12	0.293	66.09	65.08	0.085	23.55	20.62	0.470	0.165	0.161	0.139
Klang smallholding	37.56	34.69	0.352	63.70	62.22	0.118	13.68	10.44	1.050	0.202	0.199	0.160
	35.24	32.24	0.509	65.40	63.78	0.172	16.46	12.99	1.592	0.265	0.311	0.301
Tjir 1 latex from Field 31 at	49.62	46.47	0.256	64.52	62.46	0.159	30.19	27.07	0.606	0.237	0.273	0.251
RRI Expt. Station	47.68	44.42	0.353	64.12	62.10	0.161	25.74	21.65	0.758	0.303	0.272	0.249
	47.35	44.38	0.586	59.41	57.20	0.382	19.13	15.26	2.57	0.499	0.530	0.580

and clonal latex was collected and ammoniated to 0.3 per cent NH_3 before noon. Sixty gallons was centrifuged during the next morning and another 60 gallons of freshly ammoniated latex mixed with the residual 30 gallons. This procedure was repeated for seven days. VFA nos. were determined immediately before and after centrifuging and are plotted in Figure 8. It is evident that mixing of old and new field latex has a cumulative effect on the VFA no. and the quality of the concentrate.

RELATION BETWEEN VFA NO. OF FIELD LATEX, CONCENTRATE AND SKIM

Since the VFA no. of well preserved centrifuged concentrate remained sensibly constant during six months storage, it would appear that the amount of volatile acids in the concentrate depended directly on the amount of volatile acids in the ammoniated field latex. Theoretically, the VFA no. of a 60 per cent d.r.c. concentrate should be about one-third to one-half of the VFA no. of a 35 per cent d.r.c. field latex, depending on the total solids content of the latex

Table V

Recentrifuging Low Grade Concentrate

Test	Centrifuged concentrate	Recentrifuged concentrate after diluting with water
d.r.c. (%wt.)	57.76	63.87
Total solids (%wt.)	59.63	64.63
Ammonia (%wt.)	0.79	0.87
V.F.A. no.	0.18	0.07
KOH no.	0.71	0.34
Mechanical stability (seconds)	263	778
Odor after neutralization with boric acid	Slight putrefaction	Sweet

and assuming that the volatile acids are present in the serum. To investigate this, three different types of latex were collected, ammoniated to 0.3 per cent NH_3 and centrifuged after varying time intervals.

The VFA nos. were determined on the ammoniated field latex and on the concentrate and the skim after centrifuging. The results are given in Table IV and the VFA no. are compared by expressing the volatile acids as g. KOH per 100 g. serum, which is taken as 100-d.r.c. The concentration of volatile acids in the serum of the field latex does not differ significantly from that of the serum of the concentrate, suggesting that volatile acids are not associated with the rubber phase. The concentration of volatile acids in the concentrate is significantly greater than that in the serum of the skim. Moreover, this difference between concentrate and skim increases with increasing volatile acid content. This indicates that some volatile acids are removed in the sludge during centrifuging.

PURIFYING LOW GRADE CONCENTRATE

As the volatile acids are present mainly in the serum, they can be removed by dilution and reconcentration of the latex. Table V shows the improvement obtained by diluting a poor quality concentrate with water to approximately 35 per cent d.r.c. and recentrifuging.

DISCUSSION

Volatile acids in centrifuged latex concentrate have been shown to affect considerably the mechanical stability. Volatile acids develop rapidly in the field latex before centrifuging, and since their formation is attributed to contaminating micro-organisms, the first essential for the production of high quality concentrate is cleanness at all stages of preparation. The acids are produced in fresh latex and ammoniation at an adequate level should take place as soon as possible after tapping. A small quantity of formaldehyde, followed by less than the normal amount of ammonia, appeared to give good preservation of field latex. After a few days, volatile acids develop rapidly in latex ammoniated to between 0.2 and 0.5 per cent NH_3 and since between one-third and one-half of the VFA no. of the field latex is transmitted to the concentrate, it is advisable to centrifuge field latex soon after collection, preferably within twenty four hours. Newly collected latex should not be mixed with old ammoniated field latex before centrifuging. Poor quality concentrate having a high VFA no. can be purified by diluting with water and recentrifuging.

In many instances specific conductivity may be used as a means of controlling the quality of incoming field latex to be processed as concentrate, since it is related to the VFA no.

SUMMARY

A simplified procedure for determining volatile fat acids in ammoniated latex is presented. Specific conductivity can be used to indicate an approximate value of the VFA number. Volatile acids can be formed in field latex before and after ammoniating, the extent depending on a number of factors, including time of ammoniation, amount of ammonia added, and period of storage. A small amount of formaldehyde added before ammoniation delays the development of volatile acids. The VFA no. of a 60 per cent d.r.c. concentrate lies between one-third and one-half of the VFA no. of the field latex from which it is prepared, and it is shown that the presence of moderate and high concentrations of volatile acids in the concentrate is associated with inhibition of the normal increase of mechanical stability on storage. Low grade concentrate can be purified by recentrifuging and its mechanical stability increased.

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DETERMINATION OF MAGNESIUM, TOTAL PHOSPHORUS, AND FREE PHOSPHATE IN RUBBER LATEX *

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INTRODUCTION

It has been shown by Paton[1] that in latex concentrate of clone Glenshiels I, low stability and abnormal gelling characteristics are partly caused by an excess of magnesium remaining in the concentrate, due to the field latex containing too little phosphate to precipitate all the magnesium on ammoniation. Philpott and Westgarth[2] find that, in general, a low phosphorus and potassium content and a high magnesium content tend to be found in conjunction with low mechanical stability of ammoniated creamed latexes. Resing[3] has made a clonal survey of the phosphorus and magnesium contents of field latexes and finds a wide variation of the phosphorus/magnesium ratio. He has shown that a low phosphate/magnesium ratio in the field latex is correlated significantly with low mechanical stability of the concentrate. The determination of magnesium in latex concentrate is, therefore, of some importance, and since investigations concerning magnesium and ionic phosphate are complicated by the presence in latex of relatively large amounts of organic phosphate, a method for the direct determination of ionic phosphate would be advantageous.

The amounts of magnesium likely to be encountered in latex concentrate may vary from about 0.002 per cent upwards, this figure representing the solubility of magnesium ammonium phosphate in the serum. The method chosen must be capable of reasonable accuracy at this level, and so gravimetric and volumetric methods were considered less suitable than a colorimetric procedure, such as that outlined by van der Bie[4]. This method consists essentially of the precipitation of magnesium as magnesium ammonium phosphate from a solution of the latex ash, followed by dissolution of the precipitate in acid. The phosphate content of the precipitate is measured by addition of molybdic acid and reduction of the phosphomolybdic acid with stannous chloride to molybdenum blue.

In the early stages of the present investigation, it became evident that reproducible results were not consistently obtained. This was at least partly due to the fact that the final color of both the test solutions and the blank were subject to inexplicable changes. It was concluded that the method required investigation on two points:

(*a*) The precipitation of magnesium ammonium phosphate, for which Feigl[5] points out that there exists a "region of uncertain precipitation" for solutions 0.005 to 0.001 per cent with respect to magnesium and phosphate, and

(*b*) The conversion of phosphate to molybdenum blue.

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The reduction of phosphomolybdic acid to molybdenum blue is a complex reaction, the course of which depends on the nature of the reductant and the pH of the solution. Among the more common reductants that have been studied for this purpose are stannous chloride[6], hydroquinone-sulfite mixture[7], aminonaphtholsulfonic acid[8], "amidol"[9], and ferrous sulfate[10]. It has been suggested[12] that a positive error arising from a reduction of excess molybdate might result from the use of some reductants, and it was necessary, therefore, to establish the experimental conditions which would ensure a reproducible color proportional in intensity to the phosphate present.

For the determination of total phosphorus, the ashing procedure needs to be considered in the light of the subsequent formation of molbydenum blue.

The formation of molybdenum blue is of direct application to the determination of free phosphate, so that for this determination the correct conditions are required for isolating the phosphate from substances which interfere with the production or measurement of the molybdenum blue color.

EXPERIMENTAL

MAGNESIUM

1. Colorimetric measurement of orthophosphate.—The use of stannous chloride for the reduction of phosphomolybdic acid was investigated first, since, with this reagent, variable results had been obtained for determinations on latex samples. It was found that by taking a constant amount of phosphate, molybdate reagent, and stannous chloride, a range of colors could be produced by altering the acidity of the solution. A similar range of colors was produced when the phosphate was omitted entirely, so that for the range of acidities investigated the stannous chloride reduces the molybdate reagent itself. Keeping the acidity constant, solutions containing identical amounts of phosphate did not give reproducible optical densities, and there was always a variation of optical density with time. From this evidence it was decided that stannous chloride initiates a reduction which is not easily controlled, and so alternative reducing agents were considered.

The color produced by a hydroquinone-sodium sulfite reducing mixture was found to be similarly inconsistent and unreliable in a wide range of experimental conditions; nor could a consistent relationship be established between optical density and *o*-phosphate concentration.

Ferrous sulfate was the reductant finally adopted, using the method of Sumner[10]. It was found that the molybdenum blue color produced with this reagent was stable and reproducible. The effect of varying acidity was measured, and it was found that 5 drops of 5 *N* sulfuric acid in 25 ml. produced no change of optical density. Solutions of varying phosphate content were reacted with molybdate reagent and ferrous sulfate solution, and a linear relationship was found to exist between optical density and the volume of standard phosphate solution taken.

With this reductant the blank reading is small and consistent, and is accounted for by the color of the ferrous sulfate. There is a slight development of blue color on long standing, due presumably to reduction of molybdic acid, but it is not sufficient to affect the reading within thirty minutes.

2. Quantitative precipitation of magnesium ammonium phosphate.—A normal latex, free of solid magnesium ammonium phosphate, may have a magnesium content of 0.001 to 0.002 per cent, so that a 5-gram sample, which is the greatest amount of rubber that can comfortably be handled in the ashing process, gives

rise to 0.05 to 0.1 mg. magnesium. The experimental work in this section, therefore, was designed to discover whether the precipitation of this amount of magnesium is quantitative at the dilutions encountered. It was also necessary to check the stoichiometric relationship between the added magnesium and the determined phosphorus associated with it, in view of the possibility of precipitating trimagnesium phosphate instead of magnesium ammonium phosphate.

Two standard magnesium sulfate test solutions were prepared containing, respectively, 0.05 per cent magnesium (Solution A) and 0.001 per cent magnesium (Solution B). In order to determine the time required for complete precipitation, 5 ml. of solution A was added to excess sodium phosphate in the presence of ammonium hydroxide, and the precipitate was removed by filtration after two hours' standing at room temperature. The filtrate was let stand for a further sixteen hours (i.e., overnight), and any resulting precipitate was filtered off. The phosphate in both precipitates was estimated by dissolving in dilute sulfuric acid, adding acid molybdate, and reducing with ferrous sulfate. This procedure was also followed with respect to a series of 5 ml. aliquots of solution B, allowing the precipitate to stand for sixteen hours before filtration.

TABLE I

DETERMINATION OF MAGNESIUM IN STANDARD MAGNESIUM SULFATE SOLUTION

Wt. of Mg taken (mg.)	1st pptn. (mg.)	2nd pptn. (mg.)	Total (mg.)
2.49	2.44	0.09	2.53
0.0497	0.0560	—	0.0560
0.0497	0.0475	0.0045	0.0520
0.0497	0.0490	—	0.0490
0.0497	0.0490	—	0.0490
0.0497	0.0472	0.0060	0.0532
0.0497	0.0505	—	0.0505

The results are given in Table I, basing the figures on the assumption that the double phosphate is formed exclusively.

From Table I it will be seen that a standing time of two hours, as recommended by van der Bie, is in some cases inadequate. Even overnight standing was occasionally insufficient for complete precipitation, and a further slight precipitate formed on standing for twenty-four hours. The standard procedure, therefore, which was adopted for subsequent determinations was to stand overnight before filtering, and retain the filtrate for a further twenty-four hours, collecting any further precipitate.

The high recoveries of magnesium reported in the cases where two precipitates were determined separately arise no doubt from the double error involved in the two washings. This double source of inaccuracy will not occur during an actual determination.

A much larger series of precipitations was made qualitatively with the object of ascertaining whether precipitation invariably takes place under these conditions. In no case did magnesium ammonium phosphate fail to precipitate, so these conditions are outside the "region of uncertain precipitation" described by Feigl[5] and the formation of the magnesium ammonium phosphate precipitate can be relied on at the 0.05 mg. level of magnesium.

TOTAL PHOSPHORUS

The essential steps in the determination of total phosphorus are dry ashing of the sample, hydrolysis of the phosphate in the ash to the *ortho*-form, and then

conversion of the *o*-phosphate to molybdenum blue by reduction of the phosphomolybdate complex, as in the magnesium determination. The ashing procedure was investigated in relation to the final color measurement.

Following the procedure adopted by van der Bie, in which potassium nitrate was used as an ashing aid, it was found that the residual nitrous/nitric acid affects the stability of the molybdenum blue color when ferrous sulfate is used for the reduction, giving rise to a continuous increase in color with time.

TABLE 2

RECOVERY OF ADDED PHOSPHORUS

	Added P_2O_5 (%)	Total P_2O_5 found (%)	Net P_2O_5 recovered (%)
(1) Reagent blank	—	—	—
(2) Latex	—	0.082	—
(3) Latex + std. PO_4 solution	0.025	0.107	0.025
(4) Latex + std. PO_4 solution	0.050	0.130	0.048
(5) Latex + std. PO_4 solution	0.075	0.156	0.074
(6) Latex + std. PO_4 solution	0.100	0.183	0.101

Ashing with potassium nitrate was also found to be somewhat violent, and there was the further disadvantage that the presence of sodium carbonate made it difficult to control the final acidity. The use of alternative ashing aids was, therefore, investigated. These included sodium carbonate/magnesium nitrate, ammonium nitrate, and magnesium nitrate alone. Magnesium nitrate, added to the rubber sample in the form of a concentrated alcoholic solution, was found most suitable. This substance begins to decompose at a low temperature, the oxygen evolved aiding the ashing of the rubber, and a basic residue is left below the temperature at which loss of phosphorus may be expected. Using mag-

TABLE 3

TOTAL PHOSPHORUS; REPLICATE RESULTS

Sample	Phosphorus (%)
(1) Bulk shipment	0.040, 0.043, 0.040
(2) Twice centrifuged latex	0.017, 0.018
(3) Bulk shipment	0.040,0.041
(4) Twice centrifuged latex	0.016, 0.015
(5) Bulk shipment	0.036, 0.038, 0.041
(6) Electrodecanted latex	0.042, 0.046, 0.046
(7) Electrodecanted and centrifuged latex	0.018, 0.019
(8) Electrodecanted latex	0.036, 0.037
(9) Centrifuged latex	0.034, 0.036, 0.038, 0.035
(10) Twice centrifuged latex	0.015, 0.015, 0.016
(11) Centrifuged latex	0.034, 0.032, 0.034, 0.034

nesium nitrate for the ashing, the final molybdenum blue color normally remained constant in intensity, provided the ash was kept at 500° C for thirty minutes to complete the decomposition of magnesium nitrate.

The modified procedure based on the above conclusions was then used to check the recovery of phosphorus from rubber. Regular increments of phosphorus in the form of a standard phosphate solution were added to a sample of rubber latex. A control experiment showed complete recovery of phosphorus from a standard phosphate solution. The results are given in Table 2.

Using the same procedure, Table 3 shows replicate results on a number of samples, from which an idea of the reproducibility may be gained.

FREE PHOSPHATE

Phosphorus in latex appears to exist in three forms, free ionic phosphate, identifiable directly by the formation of molybdenum blue, combined phosphate, which hydrolyzes to free phosphate, giving an increase in molybdenum blue color, and protein phosphorus, which forms an integral part of the rubber/protein coagulum[11]. Direct measurement of free phosphate in latex is not possible, however, because the serum remaining after coagulation of rubber and protein gives a cloudiness with the molybdate reagent. The precipitate responsible for the cloudiness is yellow, and becomes slightly blue after reduction, and its removal by filtration leads to low and variable results for the free phosphate content, doubtless due to occlusion of molybdenum blue. In one case, however, that of a freshly redissolved freeze-dried serum, the solution remaining after coagulation of the protein remained clear on adding the molybdate reagent, and so a direct free phosphate determination could be made.

The evidence suggests that the interfering substances are uncoagulable proteins or their breakdown products, and so their removal on a cation-exchange resin was attempted, since nitrogenous material had previously been found to be removed by this means[11]. The resin, Zeokarb-215, was found to be

TABLE 4

DETERMINATION OF FREE PHOSPHATE

Sample	Resin	Phosphorus (%)
Freeze-dried serum	Zeokarb 215	0.75, 0.76
Freeze-dried serum	None	0.76, 0.79
Electrodecanted serum	Zeokarb 215	0.0077, 0.0082, 0.0082, 0.0076, 0.0081, 0.0075, 0.0080, 0.0079, 0.0079, 0.0077
Glenshiels I skim	Amberlite IR 112H	0.0028, 0.0031, 0.0030
Electrodecanted serum	Amberlite IR 112H	0.0076, 0.0075, 0.0076

effective in removing the interference in some, but not all, cases. The choice of resin is, therefore, of some importance, and a resin which on account of its pore structure retains larger ionic structures is required. The resins, Amberlite IR 112H, Dowex 50 X1, Dowex 50 X2 and Dowex 50 X4, had been found to remove most nitrogen from latex serum, and these resins proved capable of removing the interfering material for all the sera investigated.

The results of replicate determinations under a variety of conditions are given in Table 4.

The results in Table 4 provide evidence that other forms of phosphorus are not interfering with the determination. There is agreement between the results for the freeze-dried serum, with and without the use of the resin, and the values obtained for Glenshiels I skim are the minimum to be expected from the solubility of magnesium ammonium phosphate. Several other latexes tested have also shown this minimum free phosphate content of 0.002 to 0.003 per cent (as P). As direct confirmation of the noninterference of glycerophosphate, a concentrated solution of glycerophosphate was found to be unchanged with respect to its free phosphate content on passing through any of the cation-exchange resins used for the determination.

ANALYTICAL PROCEDURES

The analytical procedures adopted as a result of these investigations are outlined below.

REAGENTS

Nitric acid, d. 1.4	
Sodium acetate solution	Dissolve 50 g. hydrated salt in 100 ml. water.
Ammonium oxalate	Saturated aqueous solution.
Ammonium hydroxide d. 0.880	
Disodium hydrogen phosphate solution	Dissolve 5 g. in 100 ml. water.
Ammonium hydroxide 2 per cent. v/v	
Sulphuric acid 50 per cent. v/v.	
Ferrous sulfate solution	Dissolve 5 g. in 100 ml. 1 per cent (v/v) sulfuric acid. This solution should be freshly prepared.
Ammonium molybdate reagent	Mix equal volumes of 7.5 per cent ammonium molybdate and 10 *N* sulfuric acid.
Standard phosphorus solution A 1 ml. = 1.0 mg. P_2O_5	Dissolve 1.9159 g. dried potassium dihydrogen phosphate in water and make up to 1 liter. Add 5 ml. chloroform.
Standard phosphorus solution B 1 ml. = 10 μg. P_2O_5	Take 10 ml. standard phosphorus solution A and dilute to 1 liter.
Methyl orange indicator	
Magnesium nitrate	10 per cent solution.
Trichloracetic acid A.R.	10 per cent solution.
Amberlite IR 112H resin	
Hydrochloric acid	10 per cent aqueous solution.

MAGNESIUM

Weigh 5 g. of the dried film into a porcelain crucible, moisten with ten drops concentrated nitric acid, warm, and allow to stand for about one hour. Heat over a low bunsen flame until fuming ceases, then heat in a muffle furnace at 500° C until all carbon is removed. If necessary, raise the temperature to 700° C for a few minutes to remove the last traces of carbon. Place the crucible on a boiling water bath and digest the ash with one drop of nitric acid per 10 mg. ash in 5 ml. water for thirty minutes.

To remove calcium add 0.5 ml. sodium acetate solution and 0.5 ml. ammonium oxalate solution. Add one drop of methyl orange indicator and neutralize with concentrated ammonium hydroxide delivered from a fine jet until the indicator has almost completely changed to yellow. It may be necessary to make the final adjustment with dilute ammonium hydroxide. (Excess ammonia may cause precipitation of magnesium ammonium phosphate). Filter through a filter stick or sintered crucible after standing for 30 to 60 minutes at room temperature.

To the filtrate add 2 ml. disodium hydrogen phosphate solution and 1 ml. concentrated ammonium hydroxide, stir, and stand overnight. Filter through a sintered glass crucible or filter stick and wash twice with 5-ml. portions of dilute ammonium hydroxide. Dissolve the precipitate by running through the filter two to ten drops (depending on the amount of precipitate) of dilute sulfuric acid, rinse the apparatus with about 10 ml. water, and collect the solution in a 25-ml. standard flask. Adjust the volume to 25 ml. with water.

Transfer an aliquot of the solution containing about 0.05 mg. magnesium to a 25-ml. standard flask, add 1 ml. ammonium molybdate reagent and 5 ml. ferrous sulfate solution. Make up to volume with water. After ten minutes, transfer a portion of this solution to the cell of the Spekker absorptiometer and measure the optical density, using a red filter (Ilford No. 608).

Carry out a blank determination by mixing 1 ml. ammonium molybdate reagent and 5 ml. ferrous sulfate solution in a 25-ml. standard flask, making up to volume, and measuring the optical density of the solution as before.

Correct the reading of the test sample and determine the concentration of magnesium from a calibration curve prepared as follows.

Take a series of standard solutions containing 0 to 15 ml. of standard phosphorus solution B and add to each 1 ml. ammonium molybdate reagent and 5 ml. ferrous sulfate solution. Dilute each in a standard flask to 25 ml. and measure the optical density, using a red filter (Ilford No. 608). Construct a calibration curve plotting magnesium or phosphorus content against optical density.

$$1 \text{ mg. } P_2O_5 \equiv 0.568 \text{ mg. } MgO \equiv 0.341 \text{ mg. } Mg$$

TOTAL PHOSPHORUS

Weigh 0.1 g. of the dried film into a porcelain crucible and add to it 2 ml. of the 10 per cent alcoholic magnesium nitrate solution. Heat on a water bath until the alcohol has evaporated, then heat cautiously over a bunsen burner until distillation of the rubber is complete. Transfer to a muffle furnace and heat to 500° C for thirty minutes. If any carbonaceous residue remains, cool, add a few drops of the magnesium nitrate solution where required and heat at 500° C for a further thirty minutes. After cooling, add 5 ml. of distilled water and sufficient dilute sulfuric acid to dissolve the residue on warming. Heat for three hours on a water bath, keeping the crucible covered with a watch-glass for the first two hours. Add more water if necessary to maintain the volume. After cooling, transfer the solution to a 25-ml. standard flask, add 1 ml. ammonium molybdate reagent and 5 ml. ferrous sulfate solution. Make up to volume with water and mix well. From this point continue as in the determination of magnesium.

$$1 \text{ mg. } P_2O_5 \equiv 0.437 \text{ mg. } P$$

FREE PHOSPHATE

Weigh out 0.5 to 3.0 g. of the latex. Blow with air to remove most of the ammonia. Dilute to about 5 ml. Add 10 per cent trichloracetic acid drop by drop with swirling, until coagulation is complete. Filter through paper on to a bed of prepared Amberlite IR 112H resin of diameter about 8 mm. and height about 100 mm. (The resin should previously have been soaked in 10 per cent hydrochloric acid, washed with 10 to 20 ml. of 10 per cent hydrochloric acid, then with sufficient distilled water to remove all excess acid.) Let the filtrate run through the resin taking 5 to 10 minutes, and wash through with distilled water. Collect the filtrate in a 25 ml. graduated flask or take an aliquot portion of the filtrate. Add 1.0 ml. of molybdate reagent and 5.0 ml. of ferrous sulfate solution. Make up to 25 ml. with water. After ten minutes transfer a portion of this solution to the cell of a Spekker absorptiometer and measure the optical density using a red filter (Ilford No. 608).

Carry out a blank determination and construct a calibration curve as for the magnesium determination.

SUMMARY

A critical evaluation of the molybdenum-blue method for the determination of orthophosphate and magnesium has been made and the conditions have been

established for their quantitative determination in rubber latex. The precipitation of magnesium ammonium phosphate has been shown to be complete under the conditions of the test. For the conversion of phosphate to molybdenum blue, a comparison of several recommended reducing agents has shown that ferrous sulfate gives a stable and reproducible color which varies with the phosphate concentration according to Beer's Law. For the determination of total phosphorus, dry ashing of the sample with magnesium nitrate is proposed, followed by hydrolysis and a determination of the phosphate in the ash as molybdenum blue, as for magnesium. Free phosphate in latex serum is determined directly after coagulation and removal of interfering substances from the serum by cationic exchange.

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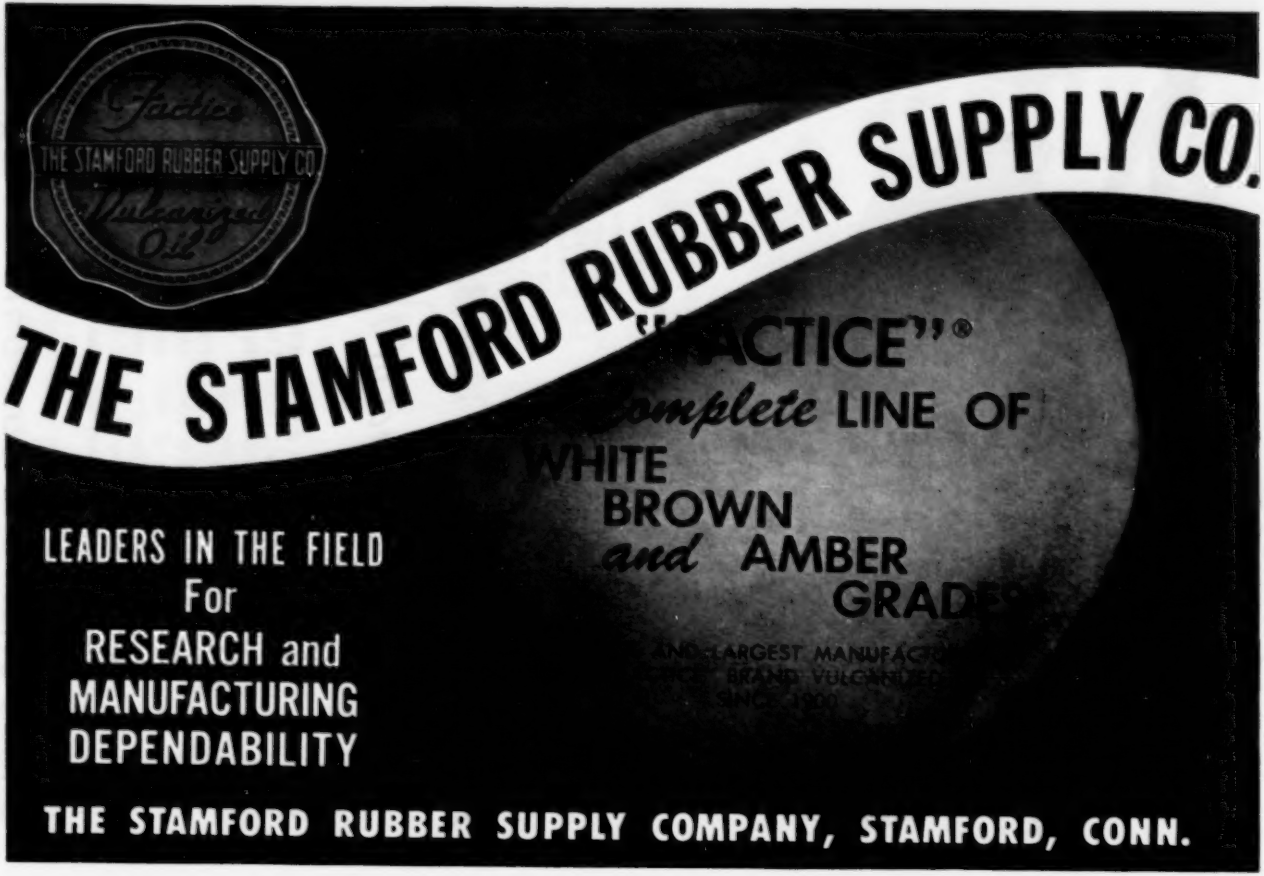
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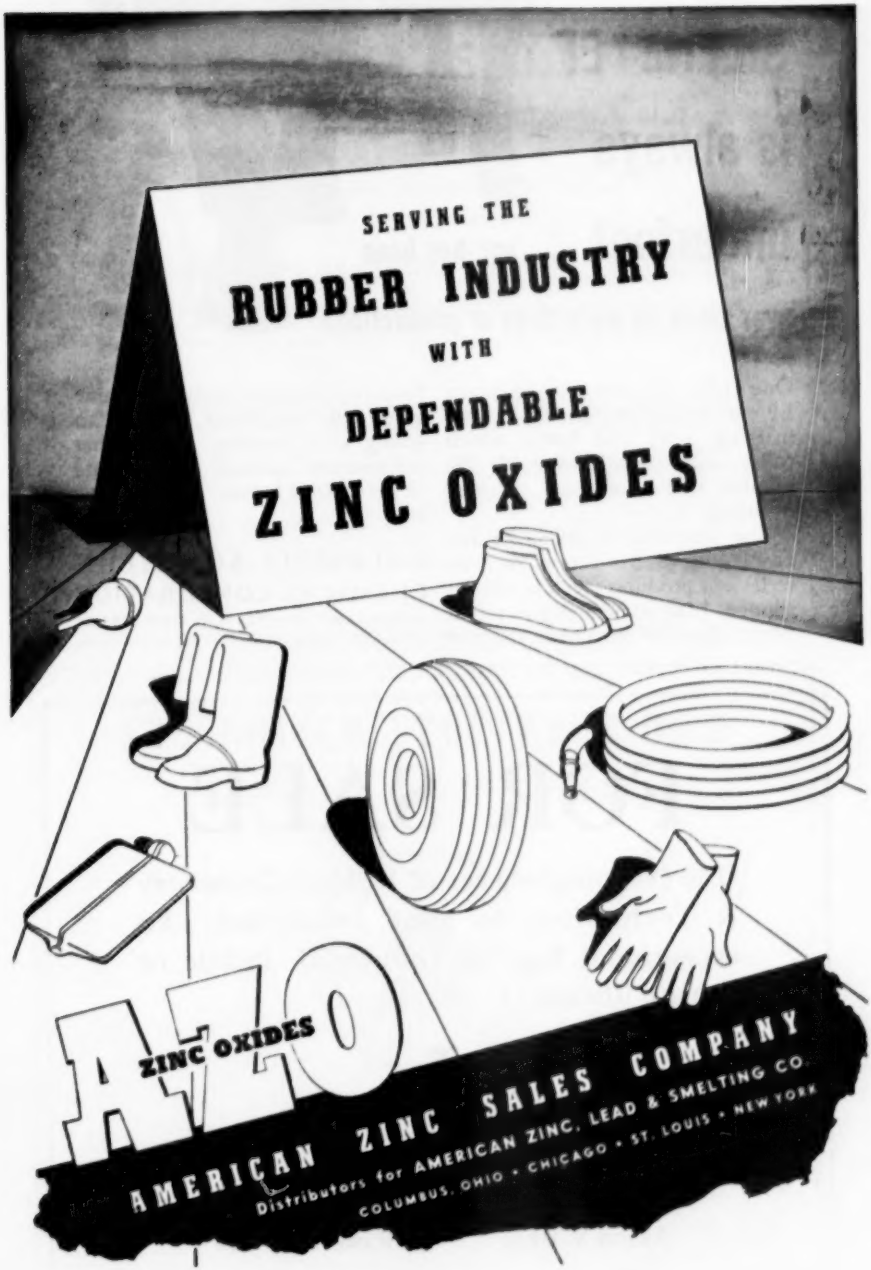
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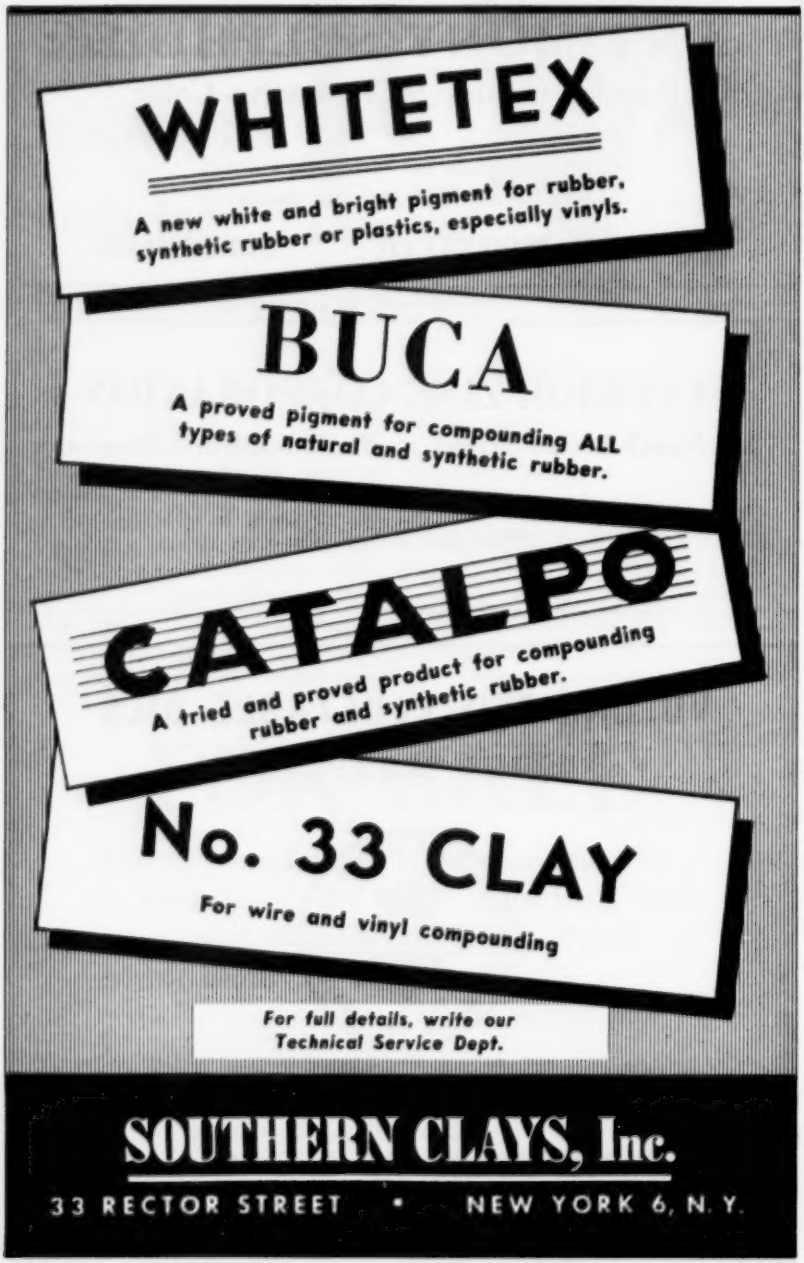
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